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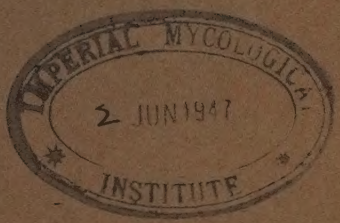

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MATHEMATICS

ON AN ANALOGY BETWEEN THE SUMMATION OF FOURIER SERIES AND THAT OF INTERPOLATION TRIGONOMETRIC POLYNOMIALS

By S. M. LOSINSKY

(Communicated by A. N. Kolmogoroff, Member of the Academy, 20. XII. 1942)

1. Let a function $f(x)$ be summable on an interval $0 \leqslant x \leqslant 2\pi$. Let

$$f(x) \sim \frac{a_0}{2} + \sum_{\nu=1}^{\infty} (a_\nu \cos \nu x + b_\nu \sin \nu x)$$

be the Fourier series of this function, and let

$$s_n(f, x) = \frac{a_0}{2} + \sum_{\nu=1}^{n} (a_\nu \cos \nu x + b_\nu \sin \nu x)$$

be the n-th partial sum of this series. We assume that $f(x)$ is continuous and has the period 2π, and denote by

$$V_n(f, x) = \frac{a_0^{(n)}}{2} + \sum_{\nu=1}^{n} (a_\nu^{(n)} \cos \nu x + b_\nu^{(n)} \sin \nu x)$$

the interpolation trigonometric polynomial of order $\leqslant n$ which coincides with $f(x)$ at the points $x_i = \frac{2\pi i}{2n+1}$ $(i = 1, 2 \ldots, 2n+1)$. Further we introduce the function

$$V_{n,t}(f, x) = \begin{cases} \dfrac{a_0^{(n)}}{2} & (\text{for } i = 0) \\ \dfrac{a_0^{(n)}}{2} + \displaystyle\sum_{\nu=1}^{t} (a_\nu^{(n)} \cos \nu x + b_\nu^{(n)} \sin \nu x) & (\text{for } i = 1, 2, \ldots, n). \end{cases}$$

It follows from the classical theorem of Fejér that

$$\lim_{n \to \infty} \sigma_n(f, x) = f(x) \text{ holds uniformly for } -\infty < x + \infty,$$

where

$$\sigma_n(f, x) = \frac{1}{n+1} \sum_{i=0}^{n} s_i(f, x).$$

Analogously, Bernstein [1] has proved that

$$\lim_{n \to \infty} V_n(f, x) = f(x) \text{ holds uniformly for } -\infty < x < +\infty,$$

where

$$V_n(f, x) = \frac{1}{n+2} \sum_{i=0}^{n} V_{n,i}(f, x).$$

Now, we introduce the functions

$$\bar{\sigma}_n(f, x) = \frac{1}{2}\left[s_n\left(f, x - \frac{2\pi}{2n+1}\right) + s_n\left(f, x + \frac{2\pi}{2n+1}\right)\right],$$

$$\bar{V}_n(f, x) = \frac{1}{2}\left[V_n\left(f, x - \frac{2\pi}{2n+1}\right) + V_n\left(f, x + \frac{2\pi}{2n+1}\right)\right].$$

Rogosinski (3) and Bernstein (2) have proved that

$$\lim_{n\to\infty} \bar{\sigma}_n(f, x) = f(x) \text{ holds uniformly for } -\infty < x < +\infty.$$

Kharchiladze (4) and Grünwald (5) have proved that

$$\lim_{n\to\infty} \bar{V}_n(f, x) = f(x) \text{ holds uniformly for } -\infty < x < +\infty.$$

Further, one can prove a set of theorems concerning the strong convergence of Fejér's sums $\sigma_n(f, x)$ (see Zygmund, «Trigonometric series»). Analogous theorems were proved by Natanson (6) fov the sums of Rogosinski, by Kharchiladze (4) for the sums $\bar{V}_n(f, x)$, and by the author (7) for the sums $V_n(f, x)$.

It is clear that the results of Bernstein and Kharchiladze—Grünwald are extensions to interpolation processes of the results obtained by Fejér and Rogosinski—Bernstein, respectively, for Fourier's series.

The aim of this note is to reveal the common source of the above-mentioned theorems of Bernstein, Kharchiladze—Grünwald and Natanson. Namely, to prove a theorem which will show that every theorem on the summation of Fourier's series can, in a certain sense, be extended to the corresponding summation of the interpolation process.

2. Let a function $M(u)$ be defined for $u \geqslant 0$ and satisfy the following conditions:

1) $M(0) = 0$, $M(u) \geqslant 0$, is convex and increases always for $0 \leqslant u < +\infty$.

2) There exists a constant $K > 0$ such that $M(2u) \leqslant KM(u)$ for $0 \leqslant u < \infty$.

3) $$\lim_{u\to 0} \frac{M(u)}{u} = 0, \quad \lim_{u\to+\infty} \frac{M(u)}{u} = \infty.$$

We denote by L^M the set of all functions $f(x)$ measurable for $0 \leqslant x \leqslant 2\pi$, for which the condition

$$\int_0^{2\pi} M[|f(x)|]\,dx < +\infty$$

is fulfilled. Then we have

Theorem. *Let*

$$\left.\begin{array}{l} k_0^{(0)} \\ k_0^{(1)}\ k_1^{(1)} \\ \cdots\cdots \\ k_0^{(n)}\ k_1^{(n)} \ldots k_n^{(n)} \\ \cdots\cdots\cdots \end{array}\right\} \tag{1}$$

be an infinite triangular matrix. We introduce for every continuous and 2π-periodic function $f(x)$:

$$\tilde{\sigma}_n(f, x) = \sum_{\nu=0}^{n} k_\nu^{(n)} s_\nu(f, x);$$

$$\tilde{V}_n(f, x) = \sum_{\nu=0}^{n} k_\nu^{(n)} V_{n,\nu}(f, x).$$

We suppose that for every continuous and 2π-periodic function $f(x)$

$$\lim_{n\to\infty} \tilde{\sigma}_n(f, x) = f(x) \text{ holds uniformly for } -\infty < x < +\infty. \tag{2}$$

Then the following statements are true:

1) $$\lim_{n\to\infty} \tilde{V}_n(f, x) = f(x) \text{ holds uniformly for } -\infty < x < +\infty \tag{3}$$

for every continuous and 2π-periodic function $f(x)$;

2) $$\lim_{n\to\infty} \int_0^{2\pi} |f(x) - \tilde{\sigma}_n(f, x)|\, dx = 0 \tag{4}$$

for every summable function $f(x)$, and

$$\lim_{n\to\infty} \int_0^{2\pi} |f'(x) - \tilde{V}_n'(f, x)|\, dx = 0 \tag{5}$$

for every absolutely continuous and 2π-periodic function $f(x)$;

3) $$\lim_{n\to\infty} \int_0^{2\pi} M\{|f(x) - \tilde{\sigma}_n(f, x)|\}\, dx = 0 \tag{6}$$

for every function $f(x) \in L^M$, where the function $M(u)$ is defined as above and

$$\lim_{n\to\infty} \int_0^{2\pi} M\{|f'(x) - \tilde{V}_n'(f, x)|\}\, dx = 0$$

for every absolutely continuous and 2π-periodic function $f(x)$ such that $f'(x) \in L^M$.

Remark. It is easy to see (Zygmund, p. 183) that the sums $\bar{\sigma}_n(f, x)$ of Rogosinski — Bernstein can be obtained from $\tilde{\sigma}_n(f, x)$ if the coefficients $k_\nu^{(n)}$ are properly chosen. The sums $\bar{V}_n(f, x)$ are obtainable from $\tilde{V}_n(f, x)$ for the same values of $k_\nu^{(n)}$.

Proof. Let

$$K_n(u) = \sum_{i=0}^{n} k_i^{(n)} D_i(u),$$

where

$$D_i(u) = \frac{\sin\left(i + \frac{1}{2}\right) u}{2 \sin \frac{u}{2}}.$$

Then, obviously,

$$\sigma_n(f, x) = \int_0^{2\pi} f(t) K_n(x - t)\, dt,$$

$$V_n(f, x) = \frac{2\pi}{2n+2} \sum_{\nu=1}^{2n+1} f(x_\nu) K_n(x - x_\nu).$$

It follows from (2) that there exists a constant $C > 0$ such that

$$\int_0^{2\pi} |K_n(x - t)|\, dt \leqslant C \quad (n = 0, 1, 2, \ldots).$$

Now we obtain, by means of a theorem by Marcinkiewicz ([6],[7]):

$$\frac{2\pi}{2n+2}\sum_{\nu=1}^{2n+1}|K_n(x-x_\nu)|\leqslant 3\int_0^{2\pi}|K_n(x-t)|\,dt\leqslant 3C,$$

and therefore

$$|V_n(f,x)|\leqslant 3C\max_{0\leqslant x\leqslant\pi}|f(x)| \qquad (n=0,\ 1,\ 2,\ \ldots;\ -\infty<x<+\infty).$$

If $T(x)$ is a trigonometrical polynomial of degree N, then it is easy to see that

$$\tilde{\sigma}_n(T,x)\equiv\tilde{V}_n(T,x) \qquad \text{for } n\geqslant N.$$

Therefore, if $f(x)$ is continuous and has the period 2π, there exists, for any given $\varepsilon>0$, a trigonometric polynomial $T(x)$ such that $|f(x)-T(x)|<\varepsilon$ for all values of x. If N is the degree of this polynomial, then

$$|f(x)-\tilde{V}_n(f,x)|\leqslant|f(x)-\tilde{\sigma}_n(f,x)|+|\tilde{\sigma}_n(f,x)-\tilde{V}_n(f,x)|=$$
$$=0(1)+|\tilde{\sigma}_n(f-T,x)|+|\tilde{V}_n(f-T,x)|<0(1)+C\varepsilon+3C\varepsilon=4C\varepsilon+0(1);$$

since $\varepsilon>0$ is arbitrarily small, the statement 1) is proved. Relative to the statements 2) and 3) it may be observed that the relations (4) and (6) can be inferred from (2) in a familiar reasoning, while the relations (5) and (7) can be proved as in ([7]).

3. It would be a simple matter to show that (2) involves the first two conditions of Toeplitz for the matrix (1):

$$\lim_{n\to\infty}k_i^{(n)}=0, \qquad \lim_{n\to\infty}\sum_{i=0}^{n}k_i^{(n)}=1.$$

Perron has propounded the question whether (2) involves the third condition of Toeplitz:

$$\lim_{n\to\infty}\sum_{i=0}^{n}|k_i^{(n)}|<+\infty.$$

We shall show that this question is to be answered in the negative. For this reason we define for each integer $n\geqslant 16$ the numbers $\lambda(n)$, $\mu(n)$ satisfying to the following conditions:

$$1\leqslant\mu(n)\leqslant\frac{n}{2},\ \mu(n) \text{ is an integer, } \lim_{n\to\infty}\frac{\mu(n)}{\lambda(n)}=+\infty,\ \lim_{n\to\infty}\frac{\mu(n)}{[\lambda(n)]^2}=0.$$

These conditions are obviously fulfilled if we take, for instance, $\lambda(n)=\sqrt{n}$, $\mu(n)=[n^{3/4}]$, where the brackets symbolize the integer part of a number. Now we define a matrix (1) in the following manner:

$$k_\nu^{(n)}=\begin{cases}\dfrac{1}{n+1}+(-1)^\nu\dfrac{1}{\lambda(n)} & \text{for } \nu=1,2,\ldots,2\mu(n)\\ \dfrac{1}{n+1} & \text{for } 2\mu(n)+1\leqslant\nu\leqslant n \text{ and for } \nu=0.\end{cases}$$

The summation method $\tilde{\sigma}_n(f,x)$ defined by means of this matrix satisfies to the condition (2). It suffices for this purpose to prove that

$$\lim_{n\to\infty}[\tilde{\sigma}_n(f,x)-\sigma_n(f,x)]=0 \text{ holds uniformly for } -\infty<x<+\infty, \qquad (7)$$

if $f(x)$ is a continuous and 2π-periodic function, and $\sigma_n(f, x)$ are Fejér's means. But it may be easily inferred from the inequalities of Schwarz and Bessel that

$$|\tilde{\sigma}_n(f, x) - \sigma_n(f, x)| = \Big| \sum_{\nu=1}^{2\mu(n)} (-1)^\nu \frac{1}{\lambda(n)} s_\nu(f, x) \Big| =$$

$$= \frac{1}{\lambda(n)} \Big| \sum_{\nu=1}^{\mu(n)} \{s_{2\nu}(f, x) - s_{2\nu-1}(f, x)\} \Big| =$$

$$= \frac{1}{\lambda(n)} \Big| \sum_{\nu=1}^{\mu(n)} (a_{2\nu} \cos 2\nu x + b_{2\nu} \sin 2\nu x) \Big| \leqslant \frac{1}{\lambda(n)} \sum_{\nu=1}^{\mu(n)} (|a_{2\nu}| + |b_{2\nu}|) \leqslant$$

$$\leqslant \frac{1}{\lambda(n)} \sqrt{\mu(n) \sum_{\nu=1}^{\mu(n)} (|a_{2\nu}| + |b_{2\nu}|)^2} \leqslant \frac{2\sqrt{\mu(n)}}{\lambda(n)} \sqrt{\sum_{\nu=1}^{\infty} (|a_\nu|^2 + |b_\nu|^2)} \leqslant$$

$$\leqslant \frac{2\sqrt{\mu(n)}}{\lambda(n)} \sqrt{\int_0^{2\pi} f^2(x)\, dx} \to 0 \text{ for } n \to \infty.$$

So (7) is fulfilled. On the other hand,

$$\sum_{\nu=0}^{n} |k_\nu^{(n)}| \geqslant \sum_{\nu=1}^{2\mu(n)} |k_\nu^{(n)}| \geqslant \frac{2\mu(n)}{\lambda(n)} - \frac{2\mu(n)}{n+1} \to \infty \text{ for } n \to \infty.$$

Therefore, the matrix $k_\nu^{(n)}$ defined by (7) fails to satisfy the third condition of Toeplitz.

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MATHEMATICS

FAMILIES OF ARCS WITH COMMON END POINTS ON THE SPHERE

By L. LUSTERNIK

(Communicated by S. L. Soboleff, Member of the Academy, 1.X.1942)

In my previous paper (1), which will be denoted by II, I have investigated upper homologies in the functional space $R = R(S_2, a, b)$ of arcs with common end points on a surface S_2 of genus O. We shall now study lower homologies and some properties of intersections and homotopies in R. In particular, we shall improve some results obtained in one of my earlier papers (2), denoted hereafter by I.

For the sake of simplicity consider the case, when S_2 is the two-dimensional Euclidean sphere. Let a and b be any pair of diametrically opposite points on S_2. Following I, consider n-dimensional pairs T_n in $R = R(S_2, a, b)$ defined as follows: denote by (φ) the meridian (semi-circle) of the sphere S_2 joining the points a and b, the longitude of which is equal to φ. T_1 is the totality of all meridians (φ) corresponding to all possible systems of values of cyclic coordinate φ. Denote further by $(\varphi_1, \varphi_2, \ldots, \varphi_{2k+1})$ the curve joining a and b formed by the following series of $2k+1$ meridians: the meridian (φ_1) directed from a to b, the meridian (φ_2) directed from b to a etc. and, finally, the meridian (φ_{2k+1}) directed from a to b. Denote by T_{2k+1} the totality of curves $(\varphi_1, \varphi_2, \ldots, \varphi_{2k+1})$ corresponding to all possible systems of values of cyclic coordinates $\varphi_1, \varphi_2, \ldots, \varphi_{2k+1}$. T_{2k} willl denote the set of curves $(\varphi_1, \varphi_2, \ldots, \varphi_{2k}, \varphi^0_{2k+1})$ where $\varphi_{2k+1} = \varphi^0_{2k+1}$ is fixed, while the other cyclic coordinates take on arbitrary values. The n-dimensional manifolds — the tori T_n — are n-dimensional Δ-cycles in R both for even and odd n.

In the subsequent we shall assume that every such Δ-cycle in R is situated in a certain R_N (R_N is a subset of R compact in itself consisting of curves, whose lengths do not exceed N). The Δ-homology of two Δ-cycles in R mean the Δ-homology of them in an R_N with a sufficiently large N.

The n-dimensional Δ-cycles T_n are dual to the ∇-cycles $\overline{Z}_n$ considered in II.

We shall generalize for the case of the functional space the notion of the «length» of a Δ-cycle introduced by Froloff and Elsholz (3) for the n-dimensional manifold. We shall say that the Δ-cycle z is of length k in R and write: $\operatorname{long}_R z = k$, if there exist k ∇-cycles $Z^1, Z^2, \ldots, Z^k$ in R such that

$$\varkappa(z, Z^1 \times Z^2 \times \ldots \times Z^k) \neq 0.$$

In what follows it will be tacitly assumed that the homologies are taken with respect to a sufficiently large modulus.

Theorem 1. $\operatorname{long}_R T_n = \left[\frac{n+1}{2}\right]$.

If the $2k$-dimensional ∇-cycle Z^{2k} is not ∇-homologous to zero in R, then it cannot be represented as the product of more than k ∇-cycles. For, if it

were not true, $Z^{2k}=U_1\times U_2\times\ldots\times U_l$, $l>k$, then we would have at least two one-dimensional «factors» among the ∇-cycles U_i, whence $U_{2k}\tilde{\nabla}0$, because the product of two one-dimensional cycles in R is ∇-homologous to zero (1). Analogously, if the $(2k+1)$-dimensional ∇-cycle Z^{2k+1} is not ∇-homologous to zero, then it cannot be represented as the product of more than $(k+1)$ ∇-cycles. Thus, every n-dimensional cycle Z^n which is not ∇-homologous to zero can be represented as the product of at most $\left[\frac{n+1}{2}\right]$ ∇-cycles. Hence

$$\log_R T_n\leqslant\left[\frac{n+1}{2}\right]. \qquad (1)$$

On the other hand, by the formulae (3) and (4) from II

$$\varkappa(T_{2k},\underbrace{Z_2\times\overline{Z}_2\times\ldots\times Z_2}_{k\text{ times}})=\varkappa(T_{2k},C_{2k}\overline{Z}_{2k})=C_{2k}\neq 0,$$

whence

$$\log_R T_{2k}\geqslant k;$$

$$\varkappa(T_{2k+1},\underbrace{Z_1\times Z_2\times Z_2\times\ldots\times Z_2}_{k\text{ times}})=\varkappa(T_{2k+1},C_{2k+1}\overline{Z}_{2k+1})=C_{2k+1}\neq 0,$$

whence

$$\log_R T_{2k+1}\geqslant k+1.$$

We see that $\log_R T_n\geqslant\left[\frac{n+1}{2}\right]$.

The only estimation for the length of T_n obtained in I by geometrical methods was $\log_R T_n\geqslant[\log_2 n]$.

Now let $\overline{S}_2$ be any surface of genus O, a_1 and b_1 denote two arbitrary points of it. We map the sphere S_2 onto $\overline{S}_2$ so that the points a and b be carried into a_1 and b_1, respectively, and the meridians on S_2 be transformed into the curves of bounded length on S_2. The families of curves T_n on R (S_2, a, b) are transformed into some families of curves $\overline{T}_n$ on $R=\overline{R}\,(S_2, a_1, b_1)$.

Denote by $[\overline{T}_n]$ the totality of the families of curves on $\overline{S}_2$ considered as subsets of $\overline{R}$ that represent the n-dimensional Δ-cycles in $\overline{R}$, Δ-homologous to $\overline{T}_n$ in $\overline{R}$. Denote further by C_n the greatest lower bound of the maxima of length of curves belonging to the families $\overline{T}_n$ on $[\overline{T}_n]$.

There exists a geodesic q_n on $\overline{S}_2$ joining a_1 and b_1, the length of which is exactly C_n.

This can be obtained by general methods of the variational calculus in the large [see, for instance, (4)]. The geodesic q_n is of index n. If $\overline{S}_2$ is a sphere and a_1, b_1 — a pair of its diametrically opposite points, then there exists a unique curve of index n that joins a_1 and b_1. Hence follows that there are no n-dimensional upper cycles in $\overline{R}$ linearly independent of T_n, i. e. for any n-dimensional Δ-cycle K_n in $\overline{R}$

$$K_n\tilde{\Delta}pT_n, \qquad (2$$

where p is an integer.

Theorem 2. *If the n-dimensional Δ-cycle U_n in $\overline{R}$ is non-homologous to zero, then for any n points $c_1, c_2, \ldots, c_n$ on $\overline{S}_2$ U_n contains a curve q passing through $c_1, c_2, \ldots, c_n$.*

Let $Z_{c_1c_2\ldots c_n}$ denote the set of curves from R passing through the points $c_1, c_2, \ldots, c_n$ in the given order (see Remark 1 in II). By (2), $K_n=pT_n$, $p\neq 0$. Hence $\varkappa(K_n, \overline{Z}_{c_1c_2\ldots c_n})=p\neq 0$ and the set-theoretical intersection $K_n\times$ $\times Z_{c_1c_2\ldots c_n}$ contains a curve q belonging to $Z_{c_1c_2\ldots c_n}$ that passes through the given points.

Definition. The family U of rectifiable curves on $\overline{S}_2$ of bounded length joining the points a_1 and b_1 is said to be *of essential dimensionality n* on $R(\overline{S}_2, a_1, b_1)$ if U, being considered as a subset of $R(\overline{S}_2, a_1, b_1)$, contains an n-dimensional Δ-cycle (or a true Δ-cycle) non-homologus to zero.

In virtue of Theorem 2 we have

Theorem 2′. *Every family of curves $K \subset \overline{R}$ of essential dimensionality n on $\overline{R}$ contains a curve passing through any n points on $\overline{S}_2$.*

Corollary. Every family of curves $K \subset \overline{R}$ of essential dimensionality $n > 2$ contains a curve possessing $\left[\frac{n}{2}\right]$ double points. Moreover, if $n = 2l$, then for any l points on the surface the family contains a curve such that its double points are the chosen ones; if $n = 2l+1$, then for any l points on the surface the family contains a subfamily of curves covering $\overline{S}_2$, the double points of which are exactly the chosen ones.

It suffices to apply Theorem 2′ at the special choice of the points $c_1, c_2, \ldots, c_n$ such that, when $n = 2l$, $c_1 = c_{l+1}$, $c_2 = c_{l+2}, \ldots, c_l = c_{2l}$, and, when $n = 2l+1$, $c_1 = c_{l+1}$, $c_2 = c_{l+2}, \ldots, c_l = c_{2l}$ and c_{2l+1} is arbitrary.

Conversely, every family of curves q in $\overline{R}$ without double points is of essential dimensionality $\leqslant 2$ and every family of curves possessing not more than l double points is of essential dimensionality $2l+1$.

In virtue of the duality in the compactum R_N for arbitrarily large N (2) implies an analogous equality for an arbirary n-dimensional upper cycle K_n:

$$K_n \tilde{\nabla} p \overline{Z}_n . \tag{3}$$

The formulae (2) and (3) determine the groups of Δ- and ∇-homologies in $\overline{R}$.

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THEORY OF ELASTICITY

MIXED PROBLEMS OF THE THEORY OF ELASTICITY INVOLVING FRICTIONAL FORCES IN RELATION TO HALF-PLANES

By L. A. GALIN

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The problem whose solution is given here is concerned with stressed state in an elastic half-plane into which one or several absolutely hard bodies (stamps) are pressed in. On the line of contact frictional forces are in action obeying the law of Coulomb. Three cases will be subjected to examination. The first deals with an isotropic body, the second, with stamps moving upon the half-plane with a constant velocity, and the third case is that of a body with arbitrary anisotropy. The boundary conditions in these problems are as follows:

$$\left.\begin{aligned} &\sigma_y = 0; \quad \tau_{xy} = 0 \qquad \text{in the interval } b_{k-1}a_k \text{ of the } x\text{-axis} \\ &\tau_{xy} = \rho_k \sigma_y; \quad v = f_k(x) \text{ in the interval } a_k b_k \text{ of the } x\text{-axis.} \end{aligned}\right\} \tag{1}$$

Here ρ_k is coefficient of friction in the k-th interval; v is vertical displacement; $f_k(x)$ is outline of the stamp in the k-th interval. The intervals $a_k b_k$, where the stamp touches the elastic body, form a totality L.

1. Isotropic body. Vertical displacement of a point of the surface is defined in the following way (1):

$$\frac{\pi E}{2(1-\sigma^2)}(v)_{y=0} = \int_{-\infty}^{+\infty} (\sigma_y)_{y=0} \lg|x-t|\,dt + \frac{1-2\sigma}{2-2\sigma}\pi \int_x^{\infty} (\tau_{xy})_{y=0}\,dt + \text{const.}$$

Here E is modulus of elasticity; σ, Poisson's coefficient. Since

$$(\tau_{xy})_{y=0} = \rho_k (\sigma_y)_{y=0} \quad \text{and} \quad (v)_{y=0} = f_k(x),$$

we have

$$\frac{\pi E}{2(1-\sigma^2)} f_k(x) = \int_{-\infty}^{+\infty} (\sigma_y)_{y=0} \lg|x-t|\,dt + \rho_k \frac{1-2\sigma}{2-2\sigma}\pi \int_x^{+\infty} (\tau_{xy})_{y=0}\,dt + \text{const.} \tag{2}$$

Let us introduce the function

$$W(z) = \int_L (\sigma_y)_{y=0} \cdot \frac{dt}{t-z} = U + iV.$$

Differentiation of the expression (2) gives the following conditions for defining $W(z)$:

$$\left.\begin{aligned} &V = 0 \qquad\qquad\qquad\qquad \text{in the interval } b_{k-1}a_k \\ &U' + \left(\rho_k \frac{1-2\sigma}{2-2\sigma}\right) V = -\frac{\pi E}{2(1-\sigma^2)} f_k'(x) \quad \text{in the interval } a_k b_k. \end{aligned}\right\} \tag{3}$$

$W(z)$ should satisfy the following conditions:

a) $W(z) \underset{z\to\infty}{\longrightarrow} \frac{N}{z}$;

b) at points a and b $W(z)$ should either be limited or have singularities of the form $(z-a)^{-\beta}$ where $0<\beta<1$. The latter condition is a consequence of the absence beneath the stamp of concentrated forces.

2. Elastic body in which stamps are moving at a constant velocity. Let w be the velocity of motion of one or several stamps. Lamé's equations for an immobile system of coordinates linked with the body are

$$(\lambda+\mu)\frac{\partial\theta}{\partial x_1}+\mu\Delta u-\delta\frac{\partial^2 u}{\partial t^2}=0;\quad (\lambda+\mu)\frac{\partial\vartheta}{\partial y_1}+\mu\Delta v-\delta\frac{\partial^2 v}{\partial t^2}=0.$$

Here λ and μ are Lamé's constants: $\theta=\frac{\partial u}{\partial x_1}+\frac{\partial u}{\partial y_1}$; δ is mass in a unit volume. These equations are satisfied if

$$u=-\frac{\lambda+\mu}{\mu}\frac{\partial^2\vartheta^*}{\partial x_1\partial y_1};\quad v=\frac{\lambda+2\mu}{\mu}\frac{\partial^2\vartheta^*}{\partial x_1^2}-\frac{\delta}{\mu}\frac{\partial^2\vartheta^*}{\partial t^2},$$

where

$$\left(\frac{\partial^2}{\partial x_1^2}+\frac{\partial^2}{\partial y_1^2}-\frac{\delta}{\lambda+2\mu}\frac{\partial^2}{\partial t^2}\right)\cdot\left(\frac{\partial^2}{\partial x_1^2}+\frac{\partial^2}{\partial y_1^2}-\frac{\delta}{\mu}\frac{\partial^2}{\partial t^2}\right)\vartheta^*=0.$$

We introduce a movable system of coordinates attached to the stamp

$$x=x_1-wt;\quad y=y_1.$$

In the new system of coordinates the stress function $\vartheta(x, y)$ satisfie the equation

$$\left[\left(1-\frac{w^2}{c_1^2}\right)\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}\right]\cdot\left[\left(1-\frac{w^2}{c_2^2}\right)\frac{\partial^2\vartheta}{\partial x^2}+\frac{\partial^2\vartheta}{\partial y^2}\right]=0. \tag{4}$$

Besides we have

$$u=m\frac{\partial^2\vartheta}{\partial x\,\partial y};\quad v=n\frac{\partial^2\vartheta}{\partial x^2}+\frac{\partial^2\vartheta}{\partial y^2};\quad \sigma_x=c\frac{\partial^3\vartheta}{\partial x^2\,\partial y}+d\frac{\partial^3\vartheta}{\partial y^3};$$

$$\sigma_y=f\frac{\partial^3\vartheta}{\partial x^2\,\partial y}+g\frac{\partial^3\vartheta}{\partial y^3};\quad \tau_{xy}=l\frac{\partial^3\vartheta}{\partial x^3}+h\frac{\partial^3\vartheta}{\partial x\,\partial y^2}.$$

Here

$$m=-\frac{\lambda+\mu}{\mu};\quad n=\frac{\lambda+2\mu}{\mu}-\frac{w^2}{c_2^2};\quad c=-(\lambda+2\mu)-\lambda\frac{w^2}{c_2^2};\quad d=\lambda;$$

$$f=(3\lambda+4\mu)-(\lambda+2\mu)\frac{w^2}{c_2^2};\quad g=\lambda+2\mu;\quad l=\lambda+2\mu-\mu\frac{w^2}{c_2^2};\quad h=-\lambda;$$

c_1 and c_2 are propagation velocities of dilatation waves and distortion waves respectively. We shall consider the case when $w<c_1$ and $w<c_2$. Equation (4) is satisfied if

$$\theta(x, y)=\mathrm{Re}\,[\Phi(z_1)+\Psi(z_2)].$$

Here

$$z_1=x+ik_1y;\quad z_2=x+ik_2y;\quad k_1=\sqrt{1-\frac{w^2}{c_1^2}};\quad k_2=\sqrt{1-\frac{w^2}{c_2^2}}.$$

Denote

$$\Phi''(z_1)=\varphi(z_1);\quad \Psi''(z_2)=\varphi(z_2).$$

Then

$$\left.\begin{aligned}\sigma_y&=i\,[G\varphi'(z_1)-G\overline{\varphi'}(\overline{z_1})+H\varphi'(z_2)-H\overline{\psi'}(\overline{z_2})]\\ \tau_{xy}&=[M\varphi'(z_1)+M\varphi'(\overline{z_1})+N\psi'(z_2)+N\overline{\psi'}(\overline{z_2})]\\ v&=2\,\mathrm{Re}\,[C\varphi(z_1)+D\psi(z_2)].\end{aligned}\right\} \tag{5}$$

Here

$$G=fk_1-gk_1^2;\quad H=fk_2-gk_2^2;\quad M=l-hk_1^2;$$
$$N=l-hk_2^2;\qquad C=n-k_1^2;\qquad D=n-k_2^2.$$

Let us compose two linear combinations from σ_y and τ_{xy}, such that from one of them $\varphi'(z_1)$ and from the other $\psi'(z_2)$ will be excluded. Multiply them by $\frac{dt}{z_1-t}$ and $\frac{dt}{z_2-t}$, respectively. Then, taking into consideration that for $y=0$ we have $z_1=z_2=z=x$ and that $\varphi'(z_1)\underset{z_1\to\infty}{\longrightarrow}\frac{N_1}{z_1}$, $\psi' z_2\underset{z_2\to\infty}{\longrightarrow}\frac{N_2}{z_2}$, we can make use of the well known properties of Cauchy integrals, and after integration over $-\infty$ to $+\infty$ obtain

$$\varphi'(z_1)=\frac{-1}{2\pi(GN-MH)}\int_{-\infty}^{+\infty}\frac{(N\sigma_y-iH\tau_{xy})_{y=0}}{z_1-t}dt;$$

$$\psi'(z_2)=\frac{1}{2\pi(GN-MH)}\int_{-\infty}^{+\infty}\frac{(M\sigma_y-iG\tau_{xy})_{y=0}}{z_2-t}dt.$$

In the case of sliding of a set of stamps the boundary conditions are as expressed by (1). Taking into account the condition $(\tau_{xy})_{y=0}=\rho(\sigma_y)_{y=0}$, we may transform the expressions for $\varphi'(z_1)$ and $\psi'(z_2)$ and integrate them with respect to z_1 and z_2, respectively. Then making use of (5) we obtain for v the following expression

$$p(v)_{y=0}=\int_L(\sigma_y)_{y=0}\lg|x-t|\,dt+q_k\int_x^{+\infty}(\sigma_y)_{y=0}\,dt+\text{const.}\qquad(6)$$

Here

$$p=\frac{-\pi[fhk_1k_2+ghk_1^2k_2^2+lf-gl(k_1^2+k_1k_2+k_2^2)]}{(l-nh)(k_1+k_2)}$$
$$q_k=\frac{\pi\rho_k[nf+fk_1k_2-lg(k_1^2+k_1k_2+k_2^2)+gk_1^2k_2^2]}{(l-nh)(k_1+k_2)}.$$

We introduce the function $W(z)=\int_L(\sigma_y)_{y=0}\frac{dt}{t-z}=U+iV$ and for its definition obtain conditions bearing complete analogy to (3):

$$\left.\begin{aligned}&V=0 && \text{in the intervals } b_{k-1}a_k\\ &U+q_kV=-pf_k'(x) && \text{in the intervals } a_kb_k\end{aligned}\right\}\qquad(7)$$

3. Anisotropic body. In a similar way the problem is solved when the body is one of arbitrary anisotropy. In this case the stresses and displacements are known to be defined as follows:

$$\sigma_y=2\,\mathrm{Re}\,[\Phi_1'(z_1)+\Phi_2'(z_2)];$$

$$\tau_{xy}=-2\,\mathrm{Re}\,[\mu_1\Phi_1'(z_1)+\mu_2\Phi_2'(z_2)];\quad v=2\,\mathrm{Re}\,[q_1\Phi_1(z_1)+q_2\Phi_2(z_2)].$$

Here μ_1, μ_2, q_1 and q_2 are complex constant numbers.

By using the method employed in the preceding section we get

$$(v)_{y=0}=A\int_L(\sigma_y)_{y=0}\lg|x-t|\,dt-\pi B\int_x^{+\infty}(\sigma_y)_{y=0}\,dt+\text{const.}$$

Moreover

$$A=-\frac{1}{2\pi}\left[-\beta_{12}\frac{\mu_1+\mu_2-\bar\mu_1-\bar\mu_2}{2}+\beta_{22}\rho\cdot\frac{1}{2}\left(\frac{1}{\mu_1\mu_2}-\frac{1}{\bar\mu_1\bar\mu_2}\right)\right]$$

$$B_k=\frac{1}{2\pi i}\left\{\beta_{12}\left[\rho_k+\frac{1}{2}(\mu_1+\mu_2+\bar\mu_1+\bar\mu_2)\right]-\beta_{22}\rho_k\cdot\frac{1}{2}\left(\frac{1}{\mu_1\mu_2}+\frac{1}{\bar\mu_1\bar\mu_2}\right)\right\}.$$

β_{12} and β_{22} are real constants.

The boundary conditions for defining the function

$$W(t)=\int_L (\sigma_y)_{y=0}\frac{dt}{t-z}=U+iV$$

in the case of a set of stamps are as follows:

$$\left.\begin{aligned} V&=0 \quad \text{in the intervals } b_{k-1}a_k;\\ AU-\pi B_k V&=f_k'(x) \quad \text{in the intervals } a_k b_k. \end{aligned}\right\} \tag{8}$$

A special problem of this type has been solved by Savin [3] (impression of a stamp into an orthotropic body in the absence of frictional forces).

4. All the examined cases lead to the particular cases of Hilbert's problem for defining $W(z)=U+iV$. We have $a(x)U+b(x)V=f(x)$, when $y=0$. Then

$$\left.\begin{aligned} &a(x)=0;\quad b(x)=1;\quad f(x)=0;\quad \alpha_{k-2,k-1}<x<\alpha_{k-1,k};\\ &a(x)=A^*;\quad b(x)=B_k^*;\quad f(x)=C^*f_k'(x);\quad \alpha_{k-1,k}<x<\alpha_{k,k+1}. \end{aligned}\right\} \tag{9}$$

The values A^*, B_k^* and C^* for each of the problems are given above; k is even; the total number of intervals is n.

The pressure of the stamp upon the elastic body is

$$p(x)=\frac{1}{\pi}\operatorname{Im}[W(x+i_0)].$$

The value of $W(z)$ satisfying the conditions a) and b) is given by the following formula:

$$W(z)=\prod_{k=1}^{n}\left(\frac{z-\alpha_{k+1,k+2}}{z-\alpha_{k,k+1}}\right)^{\mu_{k+1}+\frac{\nu_{k+1}}{\pi}}\times$$

$$\times\left\{\frac{i}{\pi}\int_{-\infty}^{+\infty}\left\{\left|\prod_{k=1}^{n-2}\left(\frac{z-\alpha_{k+1,k+2}}{z-\alpha_{k,k+1}}\right)^{\frac{-\nu_{k+1}}{\pi}}\right|\right\}_{z=x}\prod_{k=1}^{n-2}\left(\frac{x-\alpha_{k+1,k+2}}{x-\alpha_{k,k+1}}\right)^{-\mu_{k+1}}\frac{f(x)}{\sqrt{a^2(x)+b^2(x)}}\frac{dx}{z-x}+iC\right\}+$$

$$+\sum_{m=1}^{\frac{n-1}{2}}iC_m\prod_{k=1}^{n-2}\left(\frac{z-\alpha_{k+1,k+2}}{z-\alpha_{k,k+1}}\right)^{\mu_{k+1}+\frac{\nu_{k+1}}{\pi}}.$$

Besides we have here

$$\nu_{k+1}=\sum_{l=1}^{k=1}\left[\operatorname{arctg}\frac{b(\alpha_{l-1,l}+0)}{a(\alpha_{l-1,l}+0)}-\operatorname{arctg}\frac{b(\alpha_{l-1,l}-0)}{a(\alpha_{l-1,l}-0)}\right];$$

μ_{k+1} takes one of the two following values:

$$\mu_{k+1}=\left\{\begin{aligned} &-\left[\frac{\nu_{k+1}}{\pi}\right]-1;\\ &-\left[\frac{\nu_{k+1}}{\pi}\right]. \end{aligned}\right\} \tag{10}$$

To every distribution of μ there corresponds a certain value of the subscript m^*.

Among the total number of functions corresponding to all of the subscripts m^* there are $\frac{n-1}{2}$ linearly independent functions with the corresponding subscripts m. With respect to them the summation is effected. The number of solutions is in accordance with the distribution of singularities of $W(z)$ (of points where pressure takes infinite values) among α. This distribution remains indetermined when only $f(x)$ is given. If the force applied to the stamps is given along with the distribution, all C_m are equal to

zero and C is defined. If the distribution of the impressing force among $\frac{n-1}{2}$ stamps is known, then $C=0$ and the C_m are defined. Expression (10) takes a particularly simple form when there is only one stamp. Thus, when a stamp is sliding over the surface of an isotropic body, one has a solution with singularity at point b:

$$W(z)=\frac{E}{2(1-\sigma^2)}\left(\frac{z-b}{z-a}\right)^{-\theta}\int_a^b \frac{f'(\xi)}{\sqrt{1+\rho^2\frac{(1-2\sigma)^2}{(2-2\sigma)^2}}}\left|\frac{b-\xi}{\xi-a}\right|^{\theta}\frac{d\xi}{z-\xi}. \qquad (11)$$

Here

$$\theta=\frac{1}{\pi}\operatorname{arctg}\frac{(2-2\sigma)}{\rho(1-2\sigma)}.$$

Should the solution be limited at the corners of the stamp a and b, there would have to be fulfilled the condition

$$\int_a^b f'(\xi)\frac{d\xi}{(\xi-a)^{\theta}(b-\xi)^{1-\theta}}=0.$$

In that case too (11) would be the unique solution. For a single flat stamp we get the following expression for the pressure:

$$p(x)=\frac{\sin\pi\theta}{\pi}\frac{P}{\sqrt{a^2-x^2}}\left(\frac{a+x}{a-x}\right)^{\frac{1}{2}-\theta}. \qquad (12)$$

In the absence of frictional forces $\left(\rho=0 \text{ and, accordingly, } \theta=\frac{1}{2}\right)$ the well known formula of Sadovsky [4] is obtained. When two flat stamps under a force acting along the axis of symmetry are impressed in the intervals $-b<x<-a$ and $+a<x<+b$, while the frictional forces are directed to the centre, then the pressure in the interval $a<x<b$ is defined by the formula:

$$p(x)=\frac{\sin\pi\theta}{\pi}\frac{Px}{\sqrt{(x^2-a^2)(b^2-x^2)}}\left(\frac{b^2-x^2}{x^2-a^2}\right)^{\frac{1}{2}-\theta}. \qquad (13)$$

Similar expressions may be obtained in the case of an anisotropic body, as well as in that of moving stamps.

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GEOPHYSICS

EQUATION OF RADIANT ENERGY TRANSFER AS APPLIED TO PROBLEMS OF SEA OPTICS

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In the study of the light regime of the sea great interest belongs to the following magnitudes:

1. Inward flow of light at a depth z of a given wave-length λ, $F_\lambda^{(2)}(z)$.

2. Outward flow of light $F_\lambda^{(1)}(z)$. In particular, $F_\lambda^{(1)}(0)$ is responsible for the colour of sea water.

The magnitude $F_\lambda^{(2)}(z)$ has been found by Legrand ([1]) from purely geometrical considerations, without sufficient allowance being made for light scattering for the circular indicatrix of scattering.

With the help of his own method of light scattering (method of polar diagrams), Shoulejkin ([2]) has succeeded in tracing a general picture of light scattering in the sea, and in finding the magnitude of the flux that had passed through a given water layer. On the basis of Shoulejkin's formula Bashkirzeva ([3]) has plotted nomographs, serving to determine a flux after the respective depth. The magnitude of the flow of emergent light on the sea surface, $F_\lambda^{(1)}(0)$, was found in 1921 by Shoulejkin on the assumption that the decrease in light intensity with depth proceeds according to his formula, while scattering is governed by Rayleigh's law. At the same time the hypothesis has been advanced that the colour of the sea depends upon a combined action of scattering and absorption of light by water. In 1923 Gamburzev ([4]) advanced the problem of evaluating $F_\lambda^{(1)}(0)$ at a more general assumption. The solution of the problem is reduced to a system of two differential equations. Gamburzev failed to bring out the physical meaning of some of the quantities entering these equations to its full extent. This side of the problem has recently invited the attention of Kuznetzov ([5]), and the magnitudes that enter Gamburzev's equations received a clear-cut mathematical and physical meaning.

The author set before himself the aim to determine $F_\lambda^{(1)}(z)$ and $F_\lambda^{(2)}(z)$, making use of the equation of transfer of radiant energy.

With the help of these equations problems dealing with the evaluation of scattering of various order receive automatic and full solution. A precise solution of these differential equations leads to complicated integral equations. Our aim is to obtain an approximate solution, and to draw from the latter some physical conclusions.

The magnitudes $F_\lambda^{(1)}(z)$ and $F_\lambda^{(2)}(z)$ are found at the following assumptions:

1) Uniformity of scattering.

2) Constancy of the coefficient of absorption (α_λ) and scattering (σ_λ) with respect to depth.

3) Bottom albedo is put equal to zero*.

4) The light falling upon the sea surface is taken to be a diffuse or a parallel beam.

In the subsequent allowance is made for non-uniformity of scattering.

Under these conditions the equations of radiant energy transfer can be written in the shape (6):

$$\left.\begin{aligned} \frac{dF_\lambda^{(1)}(\tau)}{d\tau} &= -pF_\lambda^{(1)}(\tau) - qF_\lambda^{(2)}(\tau) \\ \frac{dF_\lambda^{(2)}(\tau)}{d\tau} &= pF_\lambda^{(2)}(\tau) + qF_\lambda^{(1)}(\tau) \end{aligned}\right\} \qquad (1)$$

where $\tau = \int_0^z c_\lambda \rho(z)\, dz$; $\rho(z)$ is the water density at a depth z; $\tau = 0$ at the sea surface and $\tau = \tau^*$ at the bottom. Moreover,

$$p = m\left(\frac{\sigma_\lambda}{2c_\lambda} - 1\right),$$

$$q = \frac{\sigma_\lambda m}{2c_\lambda};$$

$c_\lambda = \alpha_\lambda + \sigma_\lambda$ is the coefficient of extinction. The magnitude of m is the mean magnitude of sec θ**.

System (1) is to be solved under the following boundary conditions:

$$F^{(1)}(\tau^*) = 0, \quad F^{(2)}(0) = \pi I_\lambda^{(s)}.$$

The solution of this system can be written in the following convenient form:

$$F_\lambda^{(1)}(\tau) = \pi I_\lambda^{(s)} \frac{\sigma_\lambda}{c_\lambda (1+k_\lambda)^2} e^{-mk_\lambda \tau} - \frac{2\pi I_\lambda^{(s)} \frac{\sigma_\lambda}{c_\lambda} [2k_\lambda \operatorname{ch} mk_\lambda \tau + (1+k_\lambda^2) \operatorname{sh} mk_\lambda \tau]}{(1+k_\lambda)^2 e^{2mk_\lambda \tau^*} - (1-k_\lambda)^2}. \qquad (2)$$

$$F_\lambda^{(2)}(\tau) = \pi I_\lambda^{(s)} e^{-mk_\lambda \tau} - \frac{2\pi I_\lambda^{(s)} (1-k_\lambda)^2 \operatorname{sh} mk_\lambda \tau}{(1+k_\lambda)^2 e^{2mk_\lambda \tau^*} - (1-k_\lambda)^2} \qquad (3)$$

where $k_\lambda = \sqrt{\frac{\sigma_\lambda}{c_\lambda}}$.

The first terms of formulae (2) and (3) express the magnitude of the fluxes for an infinitely deep sea. Hence it is evident that the physical constants being the same, the magnitude of a flux for an infinitely deep sea exceeds the magnitude of fluxes for a sea of finite depth. From the formulae (2) and (3) it follows that the extinction of flux for an infinitely deep sea obeys the exponential law and has an index of extinction different from that which is usually adopted (law of Bouger, formula of Shoulejkin).

From formula (2) we obtain an approximate expression for the emergent flow of light on sea surface:

$$F_\lambda^{(1)}(0) \approx \pi I_\lambda^{(s)} \frac{\sigma_\lambda}{c_\lambda (1+k_\lambda)^2}$$

* This point is stipulated solely for the sake of simplicity of the formulae derived.

** The magnitude of m is usually assumed to be equal to 2 or 3/2, etc.

with an error equal to $\frac{4\pi I_\lambda^{(s)} k_\lambda \frac{c_\lambda}{c_\lambda}}{(1+k_\lambda)^2 e^{2mk_\lambda \tau^*} - (1-k_\lambda)^2}$.

Thus, the magnitude of the emergent flow of light in the case of a sufficiently deep sea is almost independent of the magnitude of m.

The following two examples may serve as an illustration to formulae (2) and (3). The depth of the reservoir is chosen equal to 10 m; the magnitude of $m=2$.

Let us construct the spectrum of extinction for a flux of emergent light at a depth of 5 m. The coefficients for optically pure water are chosen according to Aufsass ([2]). The scattering coefficient is taken in the form $\sigma_\lambda = \frac{a}{\lambda^4}$ in

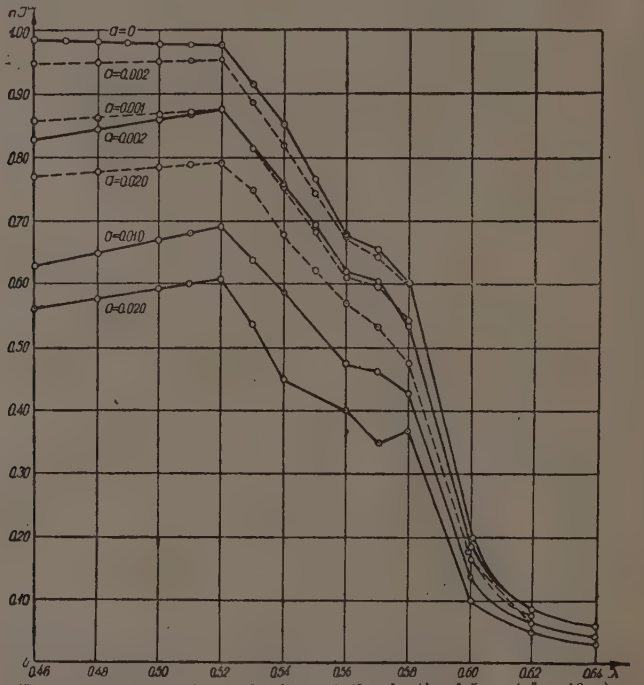

Fig. 1. Spectrum of a light flux at the depth of 5 m ($\tau^* = 10 c_\lambda$);
——— $\sigma_\lambda = \frac{a}{\lambda^4}$; — — — $\sigma_\lambda = \frac{a}{\lambda^{1.5}}$

the first case, and in the form $\sigma_\lambda = \frac{a}{\lambda^{1.5}}$ in the second; $a=0.002$; $a=0.010$; $a=0.020$ in correspondence to the depth of the vanishing of Secci disk.

In Fig. 1 are given the results of these calculations for the relation between the intensity of a flux penetrating to a depth of 5 m, and the intensity at the surface. As may be seen from this graph, the character of these curves scarcely varies with the index of λ^n.

Fig. 2 shows the results of calculations for an emergent light flux (with respect to a flux falling on the surface) for the total water thickness of the reservoir. The maximum magnitude of the flux in the visible part of the spectrum corresponds to the shortest wave-lengths.

Let us investigate analytically the run of spectral lines for an emergent light flux at the surface $F_\lambda^{(1)}(0)$ or $\Phi_\lambda^{(1)}(0) = \frac{F_\lambda^{(1)}(0)}{\pi I_\lambda^{(s)}}$.

From formula (2) it is readily obtained that

$$\Phi_\lambda^{(1}(\tau) = \frac{\sigma_\lambda \operatorname{sh} mk_\lambda(\tau^* - \tau)}{c_\lambda [2k_\lambda \operatorname{ch} mk_\lambda \tau^* + (1 + k_\lambda^2) \operatorname{sh} mk_\lambda \tau^*]}. \qquad (4)$$

This formula makes it possible to approach the explanation of sea colour. If sea colour is to be put down to the effect of absorption alone, and the sea thus to be considered as a purely absorbing medium, then $\Phi_\lambda^{(1)}(\tau) \equiv 0$. If it is to be accounted for only by the effect of scattering and, consequently, the sea to be considered a purely dispersing medium, it is no difficult

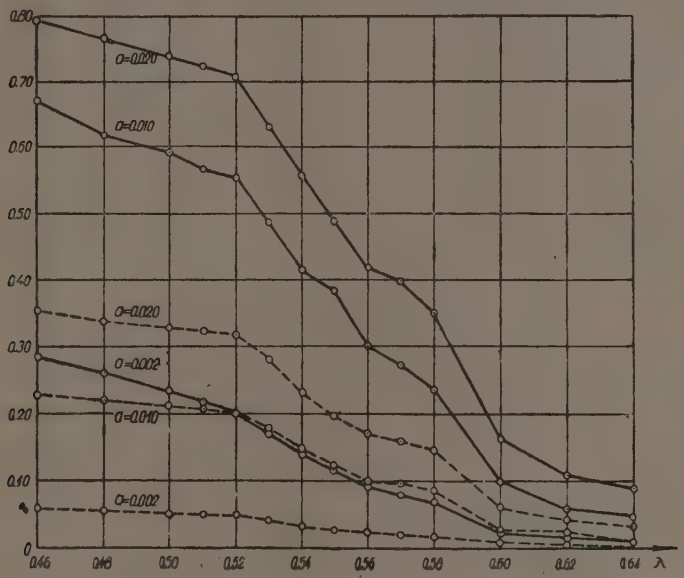

Fig. 2. Spectrum of a flux of emergent light (with respect to that falling upon the surface $\frac{F_\lambda^{(1)}(0)}{F_\lambda^{(2)}(0)}$); ——— $\sigma_\lambda = \frac{a}{\lambda^4}$; — — — $\sigma_\lambda = \frac{a}{\lambda^{1.5}}$

matter to find that $\Phi_\lambda^{(1)}(0) = \frac{m\tau^*}{m\tau^* + 2}$. The shape of the spectrum is, evidently, with τ^* sufficiently great, incompatible with the variability in the colouring of the sea surface. As has been pointed out above, Shoulejkin (2) explains the spectrum of emergent light by the joint effect of absorption and scattering actually observed. Let us examine the shape of the spectral curves for the case when α_λ and σ_λ are not equal to zero, confining ourselves to an infinitely deep sea only. Then from formula (2) it follows:

$$\left.\begin{aligned} \Phi_\lambda^{(1)}(0) &= \frac{\frac{\sigma_\lambda}{\alpha_\lambda}}{\left(1 + \sqrt{1 + \frac{\sigma_\lambda}{\alpha_\lambda}}\right)^2} \\ \text{and} \\ \frac{d\Phi_\lambda^{(1)}(0)}{d\lambda} &= \frac{1}{\left(1 + \sqrt{1 + \frac{\sigma_\lambda}{\alpha_\lambda}}\right)^2 \sqrt{1 + \frac{\sigma_\lambda}{\alpha_\lambda}}} \frac{d\left(\frac{\sigma_\lambda}{\alpha_\lambda}\right)}{d\lambda}. \end{aligned}\right\} \qquad (5)$$

The first multiplier of the expression for the derivative is always a positive one.

If $\sigma_\lambda = \frac{a}{\lambda^n}$ and the absorption spectrum is described by an empirical curve, say, of the form $\alpha_\lambda = b\lambda^p$, with $b > 0$, $p > 0$ (α_λ being an increasing function of λ), then $\frac{d\left(\frac{\sigma_\lambda}{\alpha_\lambda}\right)}{d\lambda}$ will be a negative quantity. Hence it can be concluded that $\Phi_\lambda^{(1)}(0)$ is a decreasing function of λ, i. e. $\Phi_\lambda^{(1)}(0)$ will have large values with small λ.

Thus, the colour prevalent in the spectrum of a flow of emergent light, unlike that of an inward flow, will be the violet and the blue.

Till now we assumed scattering to be uniform. Now let us make clear the influence of the non-uniformity of scattering on the magnitude of the emergent light flow.

Kuznetzov (7) has found that in case the indicatrix of scattering has the shape $\frac{1}{1+\frac{1}{3}q}[1+p_\lambda \cos\theta + q_\lambda \cos^2\theta]$, $m_\lambda^{(1)} = m_\lambda^{(2)}$, non-spherical scattering may be treated as a spherical one with an altered scattering coefficient, determined from the formula:

$$\sigma_\lambda' = \sigma_\lambda\left[1 - \frac{p_\lambda}{2m_\lambda\left(1+\frac{1}{3}q_\lambda\right)}\right].$$

The above can be examplified by the results of Shoulejkin's (2) calculation for the scattering indicatrix for the case $\frac{2\pi\rho}{\lambda} \to \infty$. We chose the interpolation formula in the form:

$$\gamma = 0.43\,[1 + 4\cos\theta + 4\cos^2\theta].$$

Hence we obtain σ_λ' putting the magnitude $m = 2$:

$$\sigma_\lambda' = 0.57\,\sigma_\lambda,$$

i. e. the scattering coefficient becomes nearly its half.

From formula (5) it can easily be found that:

$$\Phi_\lambda^{(1)}(0) > \overline{\Phi}_\lambda^{(1)}(0)$$

where $\overline{\Phi}_\lambda^{(1)}(0)$ is the emergent flux for non-spherical scattering.

Non-spherical scattering is thus found to reduce the magnitude of the emergent flux, as compared to the spherical scattering.

Let us examine the case when the light which falls upon the sea surface is directed in the form of a parallel beam.

System (1) must now be solved under different boundary conditions both with regard to intensity and fluxes; the solutions obtained will differ from one another. The boundary conditions will be given in the following shape:

$$F_\lambda^{(1)}(\tau^*) = 0, \quad F_\lambda^{(2)}(0) = \pi s_\lambda \cos\xi.$$

We have

$$F_\lambda^{(1)}(\tau) = \frac{\pi s_\lambda \frac{\sigma_\lambda}{c_\lambda}\cos\xi \operatorname{sh} mk_\lambda(\tau^* - \tau)}{2k_\lambda \operatorname{ch} mk_\lambda\tau^* + (1+k_\lambda^2)\operatorname{sh} mk_\lambda\tau^*} \tag{6}$$

$$F_\lambda^{(2)}(\tau) = \frac{\pi s_\lambda \cos\xi\,[2k_\lambda \operatorname{ch} mk_\lambda(\tau^* - \tau) + (1+k_\lambda^2)\operatorname{sh} mk_\lambda(\tau^* - \tau)]}{2k_\lambda \operatorname{ch} mk_\lambda\tau^* + (1+k_\lambda^2)\operatorname{sh} mk_\lambda\tau^*}. \tag{7}$$

Let us plot isolines (isophotos) for an infinitely deep sea $F_\lambda^{(2)}(\tau)$. Having found the limit of expression (7) with $\tau^* \to \infty$, we obtain $\Phi_\lambda^{(2)}(\tau) =$

$= \frac{F_\lambda^{(2)}(\tau)}{\pi s_\lambda} = \cos\xi e^{-mk_\lambda\tau}$; putting $\Phi_\lambda^{(2)}(\tau) = A$ and assuming water density constant and equal to unity, we find

$$z = \frac{1}{m\sqrt{\alpha_\lambda c_\lambda}} \ln \frac{\cos\xi}{A}. \qquad (8)$$

The first multiplier of expression (8) depends on the wave-length only, and gives but a scale change for the depth z.

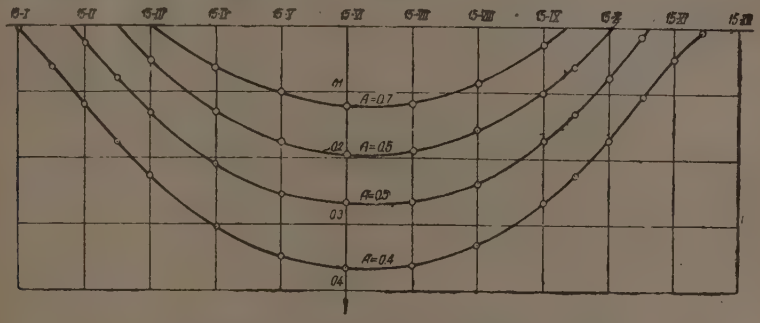

Fig. 3. Run of the isolines (according to months)

The second multiplier gives a typical picture of the run of isolines according to season.

Fig. 3 represents the isolines for various seasons. These curves are much alike analogous curves obtained from observations carried out along the southern coast of England (8). Their shape is not affected by the non-uniformity of scattering.

In concluding it is a pleasant duty to express our gratitude to Prof. E. S. Kuznetzov for a number of valuable suggestions made in the course of the present work.

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CHEMISTRY

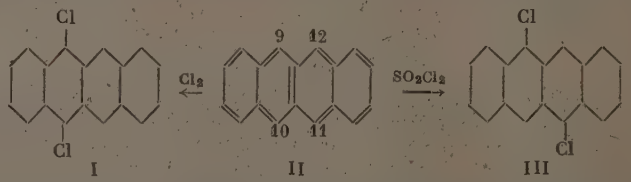
ON THE CHEMISTRY OF NAPHTHACENE. ON MESODICHLORONAPHTHACENE

By I. J. POSTOVSKY and R. G. BEYLES

(Communicated by A. E. Porai-Kochitz, Member of the Academy, 29. XII. 1942)

Naphthacene, a linear 4-nuclei hydrocarbon (tetracene, 2, 3-benzanthracene) (I) is endowed with peculiarities that have more than once been the subject of investigation (1). The hydrocarbon gold-orange in colour brings about coloration and fluorescence in other hydrocarbons (anthracene and chrysene) even when present in extremely small amounts; it shows clearly the phenomenon of thermochromy, its absorption spectrum closely approaches that of the polyene crocetylene (2) and, in spite of the presence in its structure of configurations of naphthalene and anthracene, connected with considerable unsaturation, gives no molecular compounds either with picric and styphnic acids or with trinitrobenzene. Its angular isomer, 1,2-benzanthracene, is colourless and forms easily picrate and styphnate.

The chlorination of naphthacene with sulphuryl chloride does not yield the expected mesodichloride (II), the yellow anadichloride (III) being formed instead (3).



I II III

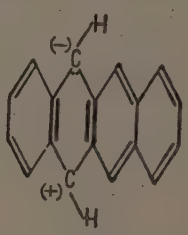
All these properties of naphthacene give reasons to believe that in the quantum mechanical superposition of different structures along to the main, unexcited structures * an important rôle in the relations of this hydrocarbon belong to those resonance structures in which the pairs of mesocarbon atoms 9, 10 (and 11, 12) and 9, 11 (and 10, 12) can be considered as almost three-valent ones. In these structures the mesocarbons have the character of free radicals, or approach interionized state which in the limit state can be expressed by formulae IV and V.

Structures IV and V have the same number of electrons that can form bonds in a different way; the total number of resonance structures that is possible for them is therefore the same. Notwithstanding the greater distance between atoms 9 and 11 as compared to that between 9 and 10, state V seems to be

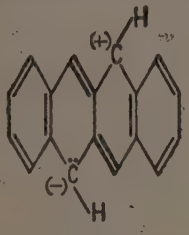
* 5 main unexcited structures have been computed for naphthacene, and besides 4857 structures of various degree of excitation. For the isomeric 1,2-benzanthracene 7 main structures have been computed and 4855 structures of various degree of excitation (4).

comparatively stable at the expense of complete symmetry and of a continuous conjugation of bonds. This may possibly account for the ease with which the anadichloride III is formed under the action of sulphuryl chloride on naphthacene.

The reaction follows a different course when naphthacene is chlorinated with chlorine at a temperature of $-15°$ in an solution of tetrachloroethane. In this case at first a rather unstable colourless addition product is formed, containing four atoms of chlorine (yield 46%, temperature of decomposition 201—205°; found %: Cl 37.56; for $C_{18}H_{12}Cl_4$ calculated %: Cl 38.35). Thise addition product splits off hydrogen chloride (gradually in the air, and intensely when heated in a solvent) and is converted into a well crystallizing dichloride coloured dark-red (m. p. 220—221°; found %: Cl 23.98; for $C_{18}H_{10}Cl_2$ calculated %: Cl 23.88). In a similar way a dark-red dibromid



IV



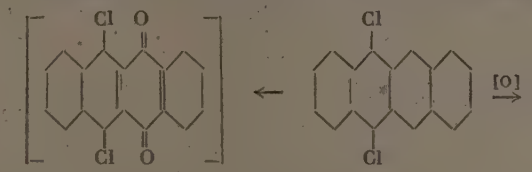
V

has been obtained (m. p. 223—225°; found %: Br 41.50; for $C_{18}H_{10}Br_2$ calculated %: Br 41.42).

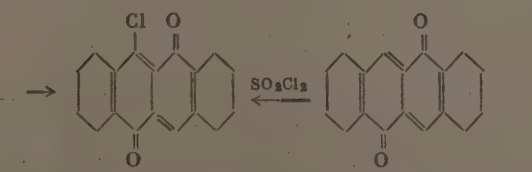
The yields of the two products after crystallization were 60 and 52%.

The heating of these dihalides with an alcoholic solution of alkali in sealed tubes at 150—160° gave alongside of naphthacene* a quinone with the characteristic properties of 9,10-naphthacenequinone (m. p. 282—283°; there is no depression of the mixed melting point). The halogen atoms are thus found to occupy the places 9, 10, i. e. the products obtained as described above are 9,10-dihalides of naphthacene.

The oxidation of the dichloride with chromic anhydride in glacial acetic acid should yield 9,10-dichloronaphthacenequinone-11,12 (VI). However, a quinone containing a single atom of chlorine is formed instead which proved to be 9-chloronaphthacenequinone-10,12 (VII), identical with the products of a careful chlorination of the anaquinone (VIII) (m. p. of 9-chloronaphthacenequinone-10,12 249—250°; there was observed no depression of the mixed melting point; found %: Cl 11.87; for $C_{18}H_9O_2Cl$ calculated %: Cl 12.12).



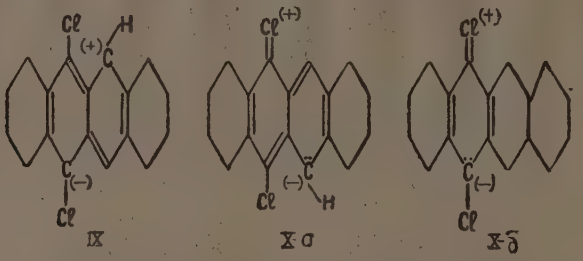
VI II



VII VIII

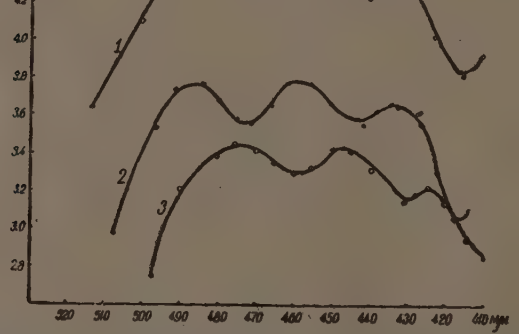
* When heated with an alcoholic solution of alkali under similar conditions naphthacene undergoes no changes.

This rather unexpected result of the oxidation reaction becomes comprehensible, if one assumes that the dichloride II participates in oxidation reactions to a considerable degree in those structures which have n o n-e q u i v a l e n t chlorine atoms, e. g. in the most polar structure IX, or in structures Xa and Xb and other structures with one bivalent positive chlorine atom*.



IX Xa Xb

In structures having the character of a 9, 10-biradical, that had been assumed by Clar (6) for naphthacene and by Fieser (7) for naphthacene derivatives (its hydroquinone), the chlorine atoms would be e q u i v a l e n t, and



Curves of the absorption spectrum of 9,10-dihaloides of naphthacene and of ananaphthacenequinone; *1* — mesodibromonaphthacene; *2* — mesodichloronaphthacene; *3* — naphthacenequinone-9,11 (ana)

oxidation in that case should lead to naphthacenequinone-9, 10 or dichloroquinone VI.

Structures IX and X, even if their rôle in the resonance system is no important one, may account for the peculiarities of the behaviour of mesodihalide derivatives of naphthacene. In connexion with this the results of spectroscopical investigation of dichloro- and dibromonaphthacene are of particular interest (see figure).

As it may be seen from the figure, the curves of the absorption spectrum *1* (for mesodichloronaphthacene) and *2* (for mesodibromonaphthacene) show a great resemblance with curve *3* — for the quinone VIII, which is known to have the same anadistribution of bond in its main structures as the mesodihalide derivative of naphthacene in structures IX and Xa.

* On bivalent positive chlorine in resonance structures see e. g. (5).

Conclusions

1. Peculiarities of the hydrocarbon naphthacene (I) are pointed out. New conditions for the synthesis of 9, 10-dichloro- and 9,10-dibromonaphthacene (II) have been found. These products are coloured red, thus differing from the yellow 9,11-dichloride (III) obtained formerly by the authors.

2. Oxidation of the 9,10-dichloride (II) instead of the 9, 10-dichloronaphthacenequinone-11, 12 (VI) expected yields a monochloronaphthacenequinone having the anastructure (VII); this points to a non-equivalence of the chloride atoms in compound II and to the probability of participation of interionized resonance structures (such as IX and X) in the oxidation reactions. In connexion with this, attention has been drawn to the likeness existing between the curves of the absorption spectrum of naphthacene derivatives and that for the anaquinone (VIII) (see figure).

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PHYSICAL CHEMISTRY

STUDIES ON THE FALLING OF FERROMANGANESE FROM ZESTAFONI WORKS

By N. N. KURNAKOV

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The first years of work in the Zestafoni ferromanganese plant* (Georgia) were marked by a number of major and minor failures. Among these was also the falling of manganese to a brown coloured powder, which was frequently observed to take place either in the workshop or after delivery to the consumer.

Lipin (1) has reported falling in a ferromanganese containing above 84% Mn. It has been noticed in general that ferromanganese alloys are not liable to collapse unless they contain 6 to 8% C and more than 82% Mn and are kept in the open.

In the Zestafoni works the ferromanganese was smelted in Siemens electrical furnaces of 7500 kVA, the charge consisting of Chiatura manganese ores, of the Motzameti limestones and of the Tkvibul coal containing 18—19% ash and about 0.2% S. The ash of this coal contained 48—50% SiO_2, 38—40% Al_2O_3, about 4% CaO and up to 1% MgO.

From 1935 onward the Tkvibul coal as the ingredient of the charge was gradually displaced by the Donetz coke containing 0.5—0.7% of moisture and 10—11% of ash. This may be seen from the data of Table 1, which have been taken from technical account of the Zestafoni plant for the period from 1934 to 1936.

Table 1

Summary of Technical Accounts of the Zestafoni Plants on Smelting of Ferromanganese

Expenditure of material in tons per 1 ton of ferromanganese	1934	Quarter					
		I 1935	II 1935	III 1935	IV 1935	I 1936	II 1936
Manganese ore	2.7	2.87	2.76	2.63	2.65	2.55	2.38
Tkvibul coal	1.2	1.25	0.90	0.36	0.31	0.235	0.075
Limestone	0.72	0.70	0.66	0.69	0.68	0.56	0.60
Iron turnings	0.27	0.19	0.18	0.16	0.16	0.175	0.19
Coke	—	0.009	0.21	0.44	0.47	0.56	0.59
Electrodes	0.040	—	0.035	0.037	0.027	0.025	0.022
Electric energy in kWh	4454	4665	4331	4270	4025	4235	3810

The falling phenomenon with the ferromanganese from Zestafoni consisted in the following: the alloy took on a dull brown colour soon after cool-

* The plant was started in October 1933.

ing and was reduced to a brownish powder, reminiscent of slags rich in lime as obtained in smelting electric and coke blast furnaces.

In 1935 the purchasing factories met with the falling of manganese supplied to them by the Zestafoni works. These were the Izhorsk plant (Leningrad), where the melt collapsed down to a dark-brown powder, and the «Serp and Molot» factory (Moscow), where it fell into cracked pieces.

According to the All-Union Standard (OST) 52-32 a normal (carbon) ferromanganese of M-type should contain 76 to 82% of Mn, and its content of C, Si, P and S should not exceed 8, 2.5, 0.4 and 0.050%, respectively.

American Society for Testing Materials (4) gives the following composition for ferromanganese, standard A 99-27: 78% of Mn at least; 7.5% of C, 1% of Si, 0.35% of P and 0.050% of S at most.

The USA federal specification for manganese published on May 26 1931 [F. S. B. No. 138 (Table 2)] sets a figure of 0.20% as the limiting content of aluminium in the B-type, which corresponds to the normal (carbon) ferromanganese of this country. In all probability this limitation was a response to the penetration to the American market of the Norwegian ferromanganese smelted in electric furnaces out of imported ores.

Table 2

Federal Specification for Ferromanganese No. 138 (USA)

Type	Mn, %	C, %	P, %	S, %	Si, %	Al, %	Fe, %
		not above					
A	Not under 95%	0.25	0.25	0.10	1.5	1.5	—
B	Not under 78%	7.5	0.35	0.050	1	0.20	Remainder

For synthetic cast iron melted in arc electric furnace Morrisson (6) reports an aluminium content ranging between 0.4 and 1.25%. Maximenko (7) has pointed out the possibility of reducing alumina by carbon in the manufacture of electrocorundum. It may be remarked that in metallurgical calculations (blast furnace smelting, steel manufacturing, etc.) no reduction of aluminium from slags or its transition into the metal is supposed to take place.

Kramarov (8) has constructed dissociation pressure curves for the oxides of aluminium, silicon, manganese, iron etc. according to the approximate formula of Nernst, as proposed by Prof. M. M. Karnaukhov (Fig. 1).

The different analyses of ferromanganese are brought together in Table 3. It may be seen from these data that the electric furnace smelting of ferromanganese at Zestafoni in 1934—1935 on a pure Tkvibul coal without admixture of coke involved the reduction of aluminium, and up to 0.5—0.6% of it—in some cases far more than that—passed into the metal; contrary to this, the ferromanganese produced in 1936 on the Donetz coke contained from 0.12 to 0.14% of Al. In a blast furnace ferromanganese the content of aluminium varies from traces to 0.10%.

Table 3

Analysis of Ferromanganese

Plant	C, %	Si, %	Mn, %	Fe, %	Al, %	P,%	Analyst
Electrotechnical Ferromanganese							
Zestafoni 1934 . .	3.26	5.68	79.69	10.22	0.47	0.19	This Institute
» 1934 . .	5.58	4.37	76.82	10.80	1.65	0.28	Do
» 1934 . .	6.27	4.39	75.87	10.77	0.50	0.28	»
Tbilissi 1934 . .	3.59	1.50	83.25	12.21	0.13	0.35	»
Zestafoni 1935 . .	7.35	1.62	79.23	11.19	0.61	0.10	»
» 1935 . .	7.45	1.75	77.14	13.28	0.14	—	»
» 1936 . .	7.62	2.77	78.89	11.16	0.12	—	»

Plant	C, %	Si, %	Mn, %	Fe, %	Al, %	P, %	Analyst
Fallen Ferromanganese (electrotechnical)							
Zestafoni 1935 . .	5.53	4.32	75.05	—	not determ	0.2	Serp and Molot
» 1935 . .	6.25	1.37	77.12	—	do	0.33	Izhorsk
» 1934 . .	5.02	1.16	81.37	10.18	0.90	0.21	This Institute
» 1935 . .	7.05	0.94	81.05	9.35	0.42	0.19	Do
» 1935 . .	5.54	1.96	79.23	10.10	0.59	0.22	Inst. of Constructions, Tbilissi
» 1935 . .	5.60	0.69	81.91	10.16	1.39	0.27	
» 1935 . .	5.56	2.39	80.60	9.13	0.69	0.30	
Blast Furnace Ferromanganese							
Makeevka	5.92	3.00	81.00	9.69	0.11	0.25	This Institute
Petrovsky (Dnepropetrovsk) . . .	6.78	1.02	74.87	17.48	0.06	0.41	Do
Konstantinov . .	7.14	0.53	78.00	not determ.	none	0.34	»
Enakievo	7.04	1.46	77.86	12.78	traces	—	»
Kraina	4.61	0.92	48.06	45.90	0.00	0.32	from the book of Iossa (6)
	5.73	1.98	50.05	43.55	0.02	0.26	
Kirov (Krasny Putilovetz) . . .	4.61	0.92	48.06	45.96	0.001	0.32	This Institute
	6.09	0.26	79.10	13.45	0.006	0.47	Do

The analysis of slags from the Zestafoni plant (Table 4) shows that in 1934 and 1935, when Tkvibul coal was used, the slags contained up to 17 and even 19 % of alumina (average, 12—14%), whereas in 1936 the transition to coke reduced the content of Al_2O_3 down to 5—6%.

Table 4

Analysis of Slag from Zestafoni Works

	SiO_2, %	CaO, %	Al_2O_3, %	MgO, %	Mn, %
Tbilissi test plant (17) . .	23.70	32.89	6.10	3.77	—
» » »	28.50	42.0	11.97	1.51	—
Zestafoni works 1934 . . .	25—27	30—32	17—19	0.45—0.65	16—19
» » 1935 . . .	31—32	34—37	13—19	—	13—16
» » 1936 . . .	30—31	30—31	5—6	3—5	19—21

Curiously enough, no falling of ferromanganese was observed on electric furnace smelting carried out in the Ferromanganese test plant at Tbilissi. It is possible that the energetic reduction of aluminium in the Zestafoni plant was due to an increased load during the «wild» phase of the three-phase electric furnace process * and to the consequent enhanced heating. In a properly controlled furnace all the three phases should have equal load.

Furthermore the ferromanganeses have been investigated for the composition and amount of gases evolving through interaction with water **.

* If the electrodes in a three-phase electric furnace are arranged in series — and this was the case at Zestafoni — the distribution of load among the phases is not uniform, and there is a «dead» phase and a «wild» phase.

** To this purpose a weighed sample of the alloy was heated with water in a flask for the collection of the evolved gas. The total analysis of gases was made with the apparatus designed in All-Union Heat Engineering Institute. The heavy hydrocarbons were estimated with the aid of the Sokolov's apparatus.

The composition of the gas was found to be 0—0.3% CO_2, 0.13—2.54% of unsaturated hydrocarbons, up to 4% O, 32—89% H, 8—40% of methane and heavy hydrocarbons. The amount of gas evolved in the reaction with water

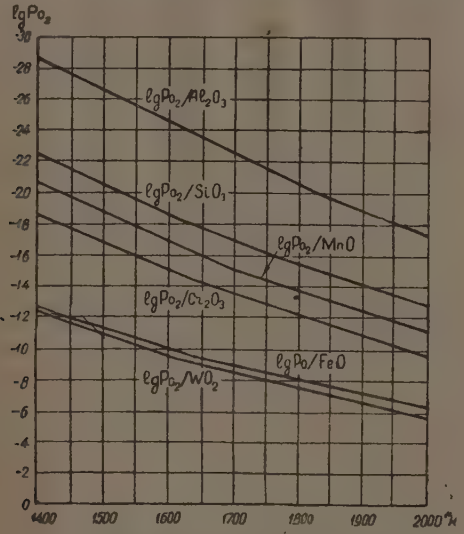

Fig. 1. Dissociation pressure of oxides of aluminium, silicon etc.

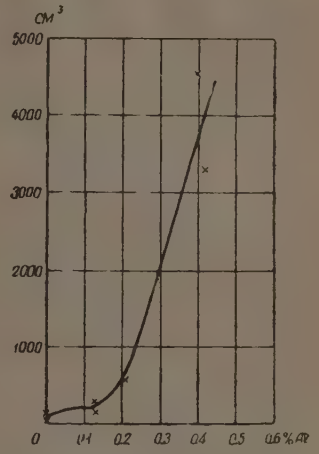

Fig. 2. Amount of gas evolved from ferromanganese on heating with water

is shown in Table 5 and in Fig. 2. It is seen to be great in the case of a ferromanganese containing above 0.2% Al.

Table 5

Amount of Gas Evolved from Ferromanganese on Heating

Name and No. of alloy	Sample, g	Water, cm³	Time of heating	Yield of gas, cm³	Content of aluminium, %
Zestafoni 1934, powder . .	40	200	4 h. 30 m.	4400	0.39
Do.	40	200	4 h. 30 m.	4430	0.39
Zestafoni 1935, powder . .	40	200	4 h. 30 m.	3150	0.42
Do.	40	200	4 h. 30 m.	3200	0.42
Konstaninov No. 8A 1936 .	40	200	4 h. 15 m.	50	none
Do.	40	200	4 h. 15 m.	50	»
Zestafoni columnar 13A 1935	40	200	4 h. 30 m.	44	»
Do.	40	200	4 h. 30 m.	50	»
Zestafoni 1935, lumps . . .	40	200	4 h. 30 m.	600	0.22
Do.	40	200	4 h. 30 m.	620	0.22
Zestafoni 1936 K 204 . . .	40	200	4 h. 30 m.	165	—
Do.	40	200	4 h. 30 m.	155	0.14

The action of humid air upon ferromanganese (80.7% Mn, 0.37% Si, 10.5% Fe, 0.6% Al and 0.28% P) has been studied by Barnabishvili [10]. He found his alloy to have turned black and brittle in response to this test. Similar results have been obtained by myself with the ferromanganese from the Makeevka works (5.92% C, 3% Si, 81.10% Mn, 9.69% Fe, 0.31% P) to which 0.35% Al has been added. The alloy when kept in a closed vessel into humid atmosphere grew gradually darker in colour and evolved a characteristic smell suggestive of decaying leaves. After two months of keeping it was transformed to a brownish powder.

The falling of the Zestafoni ferromanganese with increased content of aluminium may be interpreted as follows. Carbon enters into the alloy in the form of binary carbides of iron and manganese $(Mn, Fe)_3C$, which fact has of late been confirmed by the investigations of Khitarov [11].

Iron carbide Fe_3C plays the rôle of a binding substance and the stability of the ferromanganese depends upon it. The effect of aluminium, according to McQuaid's theory, is to increase the rate of separation of carbides from the solid solution in steel.

When present in a carbon ferromanganese, the aluminium favours the decomposition of the binary carbides of iron and manganese, weakening the bond between the particles of the alloy, whereby favourable conditions are created for the subsequent oxidation.

Similar breakdown phenomena are known in ferrosilicon — technical alloys of iron and silicon. Experiments by N. S. Kurnakov and Urasov [13], Delomenie [14], Silberstein [15], Louis [16] have shown that aluminium and its compounds promote the falling of ferrosilicon and of certain iron alloys.

In order to prevent the falling of ferromanganese care should be taken to avoid overheating on the different phases of the electric furnace while carrying on the smelting process under conditions adopted in the Zestafoni works. When the content of alumina in the charge is lowered by using instead of the Tkvibul coal alone its mixture with coke, there is less possibility for the reduction of aluminium. The content of alumina in the slag should not exceed 12—13% Al_2O_3.

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PHYSICAL CHEMISTRY

EFFECT OF TRANSFORMATION TEMPERATURE OF SUPERCOOLED AUSTENITE ON COMPOSITION OF SEPARATED CARBIDES

By N. N. SIROTA

(Communicated by N. P. Chizhevsky, Member of the Academy, 5. XII. 1942)

Regarding the isothermal transformation of a supercooled austenite of alloyed steels, it has been established, after studying this process by the methods of magnetic analysis, that the composition of the separated carbide phase varies according to the degree of supercooling. In the papers by Wever and Lange, Wever and Mathieu, Rose and Fischer experimental data have been produced showing that with decreasing transformation temperature of austenite the temperature of magnetic transformation of alloy carbides grows and approaches that for iron carbide Fe_3C. Similar relation has been reported by the present author in tempering process of quenched chrome steels (1). From these facts it may be inferred that as the higher supercooling of the austenite, the more plain is the chemical composition of the separating alloyed carbides with a tendency to decrease in carbide forming elements and to draw nearer to the composition of a pure cementite, while moving away from that corresponding to the equilibrium diagram. These facts conform to Ostwald's step rule, according to which in none of the processes the most stable state is attained at once, but first appears the neighbouring condition which is the least stable of all the possible states (2).

The theoretical interpretation of these experimental data, which it is my endeavour to give here, is based on the ideas expressed by Volmer and by Stransky and Kaishev (3) concerning crystallization processes. At the same time I shall interprete the step rule of Ostwald relative to the given case of phase transformations.

In considering the question a simple cubic crystal will be used as a model. We conceive it as an elementary cell of a carbide phase presenting a solid solution. We suppose the influence of the dissolved element in the idealized lattice to be analogous to that of the carbidogenic element dissolved in iron carbide. Besides, the carbidogenic power of the dissolved element is taken to be higher than that of iron. It will be obvious that within the limits of possible concentrations the higher the concentration of the carbidogenic element in the carbide, the stronger are the stability of the latter and its surface energy, whereas its free energy is correspondingly lower. The equilibrium concentration of carbon in austenite at the «carbide—austenite» phase boundary will decrease with increasing amounts of the element dissolved in the carbide and distributed between the two phases in a definite proportion. Suppose we have three carbides of different composition, characterized by that their content of carbidogenic element may be expressed by the inequality

$$[C]_{\mathrm{I}} < [C]_{\mathrm{II}} < [C]_{\mathrm{III}}$$

where [C] with the subscript I, II and III denotes the concentration of the carbidogenic element in the respective phase. The variations of the density and of the lattice parameter for these phases are further supposed to be negligible. Then the following relations will take place:

$$\left.\begin{array}{c} C_{\infty_I} > C_{\infty_{II}} > C_{\infty_{III}} \\ \sigma_I < \sigma_{II} < \sigma \\ F_{\infty_I} > F_{\infty_{II}} > F_{\infty_{III}} \end{array}\right\} \quad (1)$$

where C_∞ is concentration of carbon in austenite at the boundary with infinitely large crystals of the carbide phase; σ is surface energy of this phase; F_∞ is its free energy.

The surface energy σ at a face of an infinitely large crystal of the above-mentioned carbide phase is connected with concentration. We write in a simplified form

$$\ln C_\infty = -\frac{3\varphi}{KT} + \frac{5}{2}\ln T + i, \quad (2)$$

where φ is mean energy of breaking a single atomic bond; i is chemical constant; T, absolute temperature; K, Boltzman's constant.

On the other hand,

$$\sigma = \frac{\varphi}{2r_0^2}, \quad (3)$$

where r_0 is distance between the atoms.

Hence

$$\ln C_\infty = -6r_0^2\frac{\sigma}{KT} + \frac{5}{2}\ln T + i = -\alpha\frac{\sigma}{T} + \frac{5}{2}\ln T + i, \quad (4)$$

where α is a constant factor.

Expression (4) shows that the concentration of carbon in austenite at the phase boundary decreases with increasing surface energy of the carbide phase.

On the other hand, the free energy of the carbide phase F and the concentration of carbon in austenite at the phase boundary depend upon crystal size of the carbide phase. As the degree of dispersion grows, so do also the free energy of a given phase and the concentration of carbon and of the carbidogenic element in austenite at the phase boundary. According to the expression of Thomson-Freundlich, we in the most simple case have

$$RT\ln\frac{C_r}{C_\infty} = F_r - F_\infty = \Delta F = \frac{2M\sigma}{r\rho}, \quad (5)$$

where ρ is density of the carbide phase; M, its molecular weight; R, the gas constant; C_r, concentration of carbon in austenite at boundary with crystals of radius r; F_∞, free energy of the carbide phase existing in the form of infinitely large crystals; F_r, free energy of this phase consisting of crystals of radius r.

Represented graphically in $\Delta F - r$ coordinates, the equation of Thomson-Freundlich takes the shape of an equilateral hyperbola approaching asymptotically with the increase of r that value of F_∞ which characterizes the phase of a given composition.

The distance of the nearest point of the hyperbola from the origin is defined by the parametric constant K

$$K = \frac{2M\sigma}{\rho}.$$

As $\sigma_I < \sigma_{II} < \sigma_{III}$, we have the inequality

$$K_I < K_{II} < K_{III}. \quad (6)$$

In the figure the free energy of the carbide phase as a function of crystal radius r is represented graphically for the three compositions under conside-

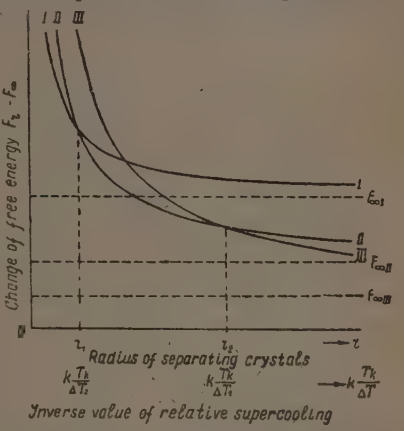
ration. In plotting the curves the ratio $\sigma_I : \sigma_{II} : \sigma_{III} = 1 : 2 : \overline{4}$ was taken as a basis.

It is seen from this plot that with a high degree of dispersion when the crystal radius is not above r_1 the carbide phase of composition I has the least free energy. This carbide phase I contains the least amount of admixture and in the case of crystals of infinitely large size has the highest free energy F_{∞_I} compared to the other two phases. For a crystal radius ranging within r_1 and r_2 the least free energy is shown by the carbide phase of composition II. When the crystal radius lies beyond r_2, the carbide phase of composition III containing the least quantity of carbidogenic element has the least free energy.

It will be apparent that on the transformation of supercooled austenite in a steel alloyed with a carbidogenic element an equilibrim carbide phase containing considerable quantities of carbidogenic element does not form, if there is no formation of large crystals.

In the case of a high dispersion the separating crystals of the carbide phase will be low in the alloy elements and the more remote from the equilibrium, as regards their chemical composition, the higher the degree of their dispersion.

If the separating carbide phase is a solid solution of the admixed element in the carbide, having a definite composition, then as the degree of dispersion decreases, there will take place a small change of concentration of the admixed element in the carbide phase. In case the carbide phase under conditions of equilibrium is a chemical compound of definite composition and forms no solid solutions, then with the increase of dispersion metastable phases will separate possessing a higher free energy. It may thus be seen that the step rule of Ostwald follows, in the case considered, from more general physical-chemical laws.



Free energy of carbide phase for compositions I, II and III as a function of crystal radius r and degree of supercooling ΔT

The critical value of the three-dimensional nuclei of the carbide phase separating in the course of the isothermal transformation of supercooled austenite depends upon the transformation temperature. Making use of Thomson-Freundlich expression (5), in which the value of the radius of the arising nucleus is connected with the degree of oversaturation $\left(\ln \frac{C_r}{C_\infty}\right)$, and of the expression (4), by means of which the carbon concentration of austenite at the boundary with infinitely large crystals of the given phase is connected with the surface energy of these crystals and with temperature, one obtains the approximate relation between the value of the radius of the three-dimensional nuclei arising upon isothermal transformation and the degree of supercooling:

$$r = \frac{2M}{\rho R \alpha} \cdot \frac{T_k}{\Delta T} = \gamma \frac{T_k}{\Delta T}. \qquad (7)$$

Here T_k is critical temperature and ΔT denotes supercooling. Hence

$$\Delta F = -R\alpha\sigma \frac{\Delta T}{T} = \beta \frac{\Delta T}{T}. \qquad (8)$$

Represented graphically in coordinates $\Delta F - \frac{T}{\Delta T}$, the equation (8) gives a family of curves like that based on equation (5).

It is evident from the figure that with supercooling exceeding ΔT_2 the phase of composition I has the least free energy. When the supercooling is higher than ΔT_1, but does not go beyond ΔT_2, the least free energy is with the phase of composition II; and, finally, in the case of low supercooling, not reaching above ΔT_1, it is the phase of composition III, i. e. the richest in carbidogenic element, according to the initial conditions (1), that has the least free energy. Hence as the temperature of isothermal transformation goes down, which means an increasing degree of supercooling ΔT, the chemical composition of the separated carbide phase includes decreasing quantities of carbidogenic element and approaches the composition of cementite.

In so far as in the process of isothermal transformation the separated carbide particles undergo coagulation, they naturally are liable to change in chemical composition. This change will be more distinct at higher transformation temperatures, because then the rate of coagulation is higher.

Conclusions

1) It has been shown on the basis of the conceptions laid down by Volmer, Stransky and Kaishev that the carbides separating on the isothermal transformation of a supercooled austenite alloyed with carbidogenic elements have the more simple composition, the higher their dispersion.

2) Now their dispersion increases as the transformation temperature goes down. Therefore with decreasing temperature of isothermal transformation the separated carbides decrease in carbidogenic elements.

3) The results obtained permit to interprete the experimental observations and at the same time offer an explanation of Ostwald's step rule relative to the here examined case of phase transformations.

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GEOCHEMISTRY

COMPOSITION OF COLLOID DISPERSION MINERALS AND THE METATHETIC CAPACITY OF GLAUCONITES FROM SARATOV*

By I. N. ANTIPOV-KARATAEV and I. D. SEDLETZKY

(Communicated by V. G. Chlopin, Member of the Academy, 5. XII. 1942)

Artificial as well as natural materials are known to vary in their efficiency as «water softeners», according to the extent to which they are able to enter into metathetic reactions with the cations of alkaline and alkaline-earth elements. The higher their absorbing power, the more they are suitable for the purposes of «softening» water. Another condition for their fitness as softeners of water is the degree of the preliminary saturation of these materials with such metathetic alkaline cations as Na. There is also a third condition — the easy percolation of water through the column of the «softener». The first condition, viz. the metathetic capacity, varies, other conditions being equal, with the mineralogical composition. It is known, for instance, that while in the case of kaolinites the metathetic capacity does not exceed 8—10 milliequivalents per 100 g of matter, it attains 30—40 milliequivalents in muscovite and amounts as high as to 80—100 milliequivalents in montmorillonite.

Prof. Nikolsky in connexion with his investigations of the metathetic power of glauconites from Lyssaya Gora (province of Saratov) turned to the authors for an X-ray mineralogical investigation of glauconite samples which he had artificially saturated with different cations (hydrogen, lithium, magnesium, sodium, barium). The preparation of the samples for the test has been carried on as follows. First, by fractional elutriation the rock was separated; then the isolated glauconite was through treatment by the corresponding chlorides saturated with different cations; and finally, the excess of salt was washed off with distilled water. The investigation of the received samples has shown that: 1) according to expectations in none of them the saturation with the different cations had changed the roentgenographic picture; both the initial and the treated samples contained the same set of colloid-dispersive minerals; 2) this set was essentially glauconite, montmorillonite and sericite. In the adjoined table the X-ray data are given for three samples of glauconite from Lyssaya Gora, province of Saratov**.

* Report delivered May 1941 at Saratov to a meeting on industrial resources of the Volga region.

** Average Composition (in %) of Glauconite from Saratov from Five Analyses

SiO_2	Fe_2O_3	Al_2O_3	CaO	MgO	FeO	K_2O	Na_2O	H_2O <110°	H_2O >110°	P_2O_5	TiO_2	CO_2	Total
50.43	20.84	6.25	1.69	2.82	traces	4.93	2.13	4.88	5.49	0.69	traces	traces	100.15

X-ray Data for Glauconite from Saratov

Glauconite $R_5'R''.R_4'''Si_8O_{35}\ ^1/_2\ 4H_2O$ (according to Pilipenko*)				Glauconite saturated with hydrogen ions				Glauconite saturated with lithium ions				
				Debye rings								
Intensity	d	Glauconite	Montmorillonite	Sericite	Intensity	d	Glauconite	Montmorillonite	Sericite	Intensity	d	Glauconite	Montmorillonite	Sericite
Strong	12.3	—	+	—	Strong	12.3	—	+	—	Strong with background	12.3	—	+	—
Strong	9.90	+	—	+	Strong	9.90	+	—	+	Do	9.58	+	—	+
Moderate	8.30	—	—	—	Moderately weak	8.29	—	—	—					
Weak, β-emission	6.70	—	—	—	Moderately weak, β-emission	6.69	—	—	—	Moderate, β-emission	6.11	—	—	—
Moderate	5.80	—	—	+	Moderate	5.80	—	—	+	Moderate	5.50	—	—	+
Strong	4.90	—	—	—	Strong	4.94	—	—	+					
Very strong	4.50	+	+	+	Very strong	4.50	+	+	+	Moderate	4.49	+	+	+
Strong	3.65	+	—	+	Moderately strong, β-emission	3.79	+	—	+	Weakly moderate	3.68	+	—	+
Strong	3.35	+	—	+	Do	3.37	+	—	+	Do	3.37	+	—	+
Weak	3.08	+	+	+	Weak	3.09	+	+	+	Do	3.09	+	+	+
Moderately weak	2.89	+	—	+	Moderately weak, β-emission	2.89	+	—	+	Weakly moderate, β-emission	2.88	+	—	+
Very strong	2.60	+	+	+	Very strong	2.61	+	+	+	Strong	2.61	+	+	+
Moderately strong	2.42	+	—	+	Moderately strong	2.42	+	—	+	Moderate	2.41	+	—	+
Weak	2.29	+	+	+	Weak	2.29	+	+	+	Weak	2.27	+	—	+
Weak	2.16	+	+	+	Weak	2.17	+	+	+	Weak	2.03	+	—	—
Weak	2.06	—	—	+	Weak	2.03	—	—	+					
Weak	1.84	+	—	+	Very weak	1.84	+	—	+	Very weak	1.84	+	—	+
										Moderate	1.67	+	+	+
										Strong	1.51	+	+	+
Weak	1.43	+	+	+	Weak	1.43	+	+	+	Weak, β-emission	1.44	+	—	+
Very weak	1.37	+	—	+	Very weak	1.38	+	—	+	Do	1.38	+	—	+
Moderate	1.32	+	+	+	Moderate	1.32	+	+	+	Moderately weak	1.31	+	+	+
Very weak	1.15	+	+	—	Very weak	1.18	+	+	—	Weak	1.26	+	+	+
Very weak	1.06	—	—	—										

* Fe Kα; 30 kV; 10 mA.

An attempt at a quantitative determination of the minerals entering into the composition of the samples, made on the basis of the obtained data, has given the following approximate figures; glauconite, 50%; montmorillonite, 40%; sericite, 10%. From this it appears that glauconite in fact contains minerals of high absorbing power (montmorillonite). The proportion of sericite as admixture is not high. Thus, the assumption of Pilipenko([1]) as to the non-uniformity of the microcrystalline mixture of minerals in the glauconite from Saratov has found confirmation. On the other hand, this mixture is not between opal, lussatite and some green-yellow mineral, as he supposed it to be.

Direct estimations of the metathetic ability in the investigated samples of glauconite have been performed in the laboratory of Nikolsky([2]). The figures obtained are not great: with pH = 9 the metathetic ability of the glauconite from Saratov is 31.08 milliequivalents per 100 g of matter (one molar solution of $BaCl_2$); the difference caused by changing the pH of the medium by one is 4.0 milliequivalents. Under similar conditions permutite showed a metathetic ability of 450 milliequivalents, and the difference due to pH fluctuations within the same amplitude was 49 milliequivalents.

Furthermore, all cations are not absorbed by the glauconite to the same extent. The absorption of sodium, for instance, is much weaker than that of calcium. In order to increase the metathetic ability of glauconite with respect to sodium, on its regeneration in water-softening columns, a treatment with slightly alkalized solutions of NaCl is necessary. Under these conditions the absorbing capacity of the glauconite with respect to sodium may be expected to reach the metathetic capacity for calcium at pH = 7.0 — 7.5. Special tests by Nasilenko ([3]) on the metathetic capacity of glauconites used in industry have also shown rather poor figures for calcium. In the most favourable cases the metathetic capacity for calcium was varying within 0.53 to 0.84% CaO, or 19 — 30 milliequivalents per 100 g of matter (analysed in Kharkov); within 0.46 — 0.57% CaO, or 16 — 20 milliequivalents (Moscow); about 0.47% CaO, or 17 milliequivalents (Sverdlovsk), glauconite from Viatka; and from 0.3 to 0.4% CaO, or from 11 to 18 milliequivalents (Leningrad).

From the fact that the investigated samples of glauconite have shown a comparatively low metathetic capacity it appears that the way to improving the quality of this raw material should be sought in the methods of its further enrichment. Careful physical-chemical investigations are necessary along this line.

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GEOCHEMISTRY

SULPHUR IN THE BUGURUSLAN OIL REGION

By G. I. THEODOROVICH

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1. In one of our preceding articles(1) we have shown on the example of the Sterlitamak — Ishimbay oil-fields that in case the rocks that form the roof of an oil deposit are though temporarily disturbed and not overlain by a gas-bearing zone, in the overlaying deposits there takes place formation of a sulphur-bearing zone or of sulphurized areas. Unlike this, if the roof of an oil-field is not disturbed by erosion, the oil is usually overlain by a gas-bearing zone and no appreciable sulphur separation is observed.

Over a considerable area of the Buguruslan oil region, corresponding to the higher parts of the Bolshe-Kinelsky uplift, in the carbonate series of the spiriferous substage the oil-bearing zone is covered by a well developed gas-bearing zone overlain in the west (Kalinovsky, Juravlevsky, Novo-Stepanovsky districts) by a packet of anhydrites over 20 — 30 m thick. In the eastern part of the region (Buguruslansky; Krasnoyarsky and Nijne-Zagladinsky districts) the anhydrites of the cover are cut by the appearing packet of rock-salt into upper (supra-salt) and lower (sub-salt) anhydrites; the total thickness of the series of hydrochemical sediments is thereby increased.

The rocks overlying the series of hydrochemical deposits, which make up the cover of the Buguruslan oil-fields, are devoid of sulphur. In the western districts of the region it is observed, however, under the anhydrite cover, in close proximity to the peripheral parts of gas and oil accumulations. Natural sulphur is found here in the southern wells which are beyond the contour of oil occurrence, in the zone of water-oil contact, mostly in the wells of the north-west direction (Pokhvistnevsky, Amanaksky and Sosnovsky plots) and occasionally in the northern wing of the Bolshe-Kinelsky uplift. The two last directions are characterized by an elevated position of the surface of the oil-bearing contact which shows a general raise towards the NNW; at the same time the possible stage of oil occurrence is reduced. Unlike this, the eastern districts (Buguruslansky, Krasnoyarsky, Nijne-Zagladinsky) which are overlain by a thicker layer of upper and lower anhydrites with an interlayer of rock-salts are totally deprived of deposits of natural sulphur. These districts are characterized by a decrease in the thickness of the carbonate series of the spiriferous substage; the series is characterized by the presence of gas and abundant inclusions of pyrite in the rocks of the terrigenous series, by which it is directly underlain. The latter is oil-bearing at places.

The middle and western parts of the region of the Buguruslan oil-fields, when viewed on a map, prove to be surrounded from south, west, north-west and north by a sulphur-bearing aureolus. The countours of the latter correspond to the rocks of the dolomite packets of the carbonate series of the

spiriferous substage, which directly underly the anhydrites of the hydrochemical series of the cover, or are separated from the latter by a rather thin packet of mergel rocks.

2. If we are to assume that in all the directions cited above the appearance of natural sulphur is connected with the proximity of the water-bearing, or more strictly speaking, oil- and water-bearing zone, then the ratio of sulphur-bearing wells, and usually the abundance of sulphur separation, is observed to increase in the N—NW direction; they coincide not only with the proximity of the water-bearing zone, but with the approach of the latter to the gas-bearing zone, which is due to an upheaval to the NNW of the water and oil contact, and to a considerable reduction of the possible stage of oil occurrence. Similar cases of formation of natural sulphur are well known to investigators of oil-gases. It has been more than once reported that if the gas-sampling proceeds in a medium open to moisture and oxygen, then the hydrogen sulphide of the oil-gas collected is entirely or partly oxidized to elementary sulphur in the course of preservation of the sample. What seems to us interesting in the observations reported above, is the intense oxidizing part that water containing dissolved oxygen is supposed to play in the process of hydrogen sulphide oxidation. The presence of moisture in the air in general or in the gaseous phase containing oxygen also contributes to the oxidation of H_2S. It is well known, on the other hand, that in similar water solutions, the SO_4'' ion is reduced to H_2S under the influence of oil-gas and fluid bitumens, in the presence of bacteria or catalysers. Hence in the formation of natural sulphur the most important place belongs to aqueous, or humid gaseous medium which in the case of original compounds offers the most favourable conditions. In the Buguruslan region natural sulphur is found in caverns and fissures of rocks composing the carbonate series of the spiriferous substage. In the former case it is accompanied with clear grained calcite, sulphur being usually present on calcite. Under the conditions described above, natural sulphur occurs along with remains of oil or hydronized oil; in the absence of these it occurs in light-coloured rocks, within the zone of approach or contact of the gas-bearing and the water-bearing zone.

3. It must be stressed that in carbonate rocks of the spiriferous substage, in the western and medium zone of the Buguruslan region, natural sulphur occurs in an anhydrite cover, along the periphery or in the sole of the edge-parts of gas-oil deposits. Spiriferous waters represent stratum waters (edge- and soil-waters) of the western areas of Buguruslan oil-fields. These waters are probably fed from a territory 4—7 km to the NNW from the region of the worked oil-fields, at the outcrop of spiriferous and partly of the conchiferous substage of the Kazan stage. The continuous afflux of these waters is probably responsible for the formation of natural sulphur under the anhydrite cover. Irrespective of the mode of migration of spiriferous waters, the absence of natural sulphur in the region of eastern districts of the Buguruslan oil-fields, in general, and under the bottom anhydrites of the geochemical series (i. e. in the carbonate series), in particular, is in agreement both with the abundance of pyrite in the rocks of the terrigenous series, and with its presence in the carbonate series.

From the above mineralogical traits of the spiriferous rocks of the eastern (more precisely, south-eastern) districts of the recent contour of the Buguruslan region, as compared to the north-western districts, it is evident that under the series of hydrochemical sediments the migration of spiriferous waters proceeds at a much lower rate, if at all. The absence of natural sulphur and the presence of pyrite point to the reducing character of the spiriferous waters in the region of the eastern districts of the Buguruslan region. In the western districts these waters are much more mobile and carry with them oxygen which, in the neighbourhood of the gas-oil accumulation, within the zone of struggle between the oxidying and reducing media, accounts for the separa-

tion of natural sulphur. It is of interest that while there is no natural sulphur at all in the eastern districts of the Buguruslan region, the southern wells sunk along the periphery of Novostepanovsky district are poor in sulphur. Westward, in the southern wells of the eastern Kalinovsky districts, natural sulphur is found in larger amounts. Farther to the NW, within the boundaries of the Amanaksk and other north-western districts, the number of sulphur separations increases, and the width of the sulphur-bearing aureolus is considerably extended.

4. Our conclusion from the above said is that if in the course of prospecting of old and search for new industrial oil deposits we run in the Buguruslan oil region across appreciable or considerable inclusions of natural sulphur in spiriferous deposits under an anhydrite cover, this should be taken as an evidence of the peripheral zone of gas-oil deposit. Every sulphur-bearing section must therefore be given due attention and the direction of the oil deposits must be determined by subsequent work. It is of interest that in the southern steep wings of the upheaval of the Bolshe-Kinelsky uplift and of those composing its continuation to the NW, natural sulphur occurs within the water-oil zone, industrial oil deposits lying directly to the NN.

In the north-west direction and in the northern part of the Bolshe-Kinelsky uplift, in connexion with the uplift to the NNW of the water-oil watershed, the possible stage of oil occurrence is reduced, and there takes place an approach between the gas-bearing and the water-bearing zone. Natural sulphur is met within the boundaries of a wide diffused aureolus.

Thus, out of the two described types of sulphur occurrence in the Buguruslan region, the former, when sulphur coincides with the water-oil zone, seems to be the most promising. In this case the existence of an industrial oil-bearing zone may be assumed in the neighbourhood of a given sulphur-bearing section.

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